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CHEMICAL CHANGES IN AN IRRIGATED SOIL DURING 28 YEARS OF DIFFERENTIAL FERTILIZATION¹

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INTRODUCTION

ONE OF THE most extensive long-term fertility trials on irrigated soils in a semiarid region is the fertilizer experiment with citrus being conducted at Riverside. The purposes of the experiment were to study the effects of a variety of fertility levels and treatments on yield, growth, and behavior of trees, to measure the cumulative and secondary effects of fertilizers on the trees, and to study the effects of fertilizers, soil amendments, and irrigation on properties of the soil. The purpose of this paper is to report changes in the chemical properties of the soil that have resulted from irrigation and differential fertilization.

DESCRIPTION OF THE EXPERIMENT

Washington Navel oranges on sweet orange rootstocks were planted for this experiment in 1917. The land had been previously dry-farmed but had not been fertilized or irrigated. During the first ten years of the growth of the trees fertilizers were not used. During this period winter covercrops of yellow bitter clover or of purple vetch were grown annually, and during the first six years, summer covercrops of cowpeas were grown. The winter covercrops used since 1927 have been dominantly vetch with barley.

In 1927, differential treatments of the plots were begun. Parker and Batchelor (1932)⁶ described the method of distributing the plots to the various treatments. Each plot consisted of a row of eight Washington Navel

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⁶ See "Literature Cited" for citations referred to in the text by author and date.

TABLE 1

DESCRIPTION OF CHEMICAL TREATMENTS USED IN THE PERIOD
1939-40 UNTIL THE TIME OF SAMPLING IN 1955. DURING 1927
TO 1939 THE TREATMENTS WERE ESSENTIALLY THE SAME
EXCEPT THAT THE RATE OF APPLICATION OF N WAS
130 POUNDS PER ACRE

Treatment number	Nitrogen		Phosphorus, lbs P ₂ O ₅ /A	Potassium, lbs K ₂ /A	Amendments and/or covercrop
	lbs N/A	Source			
1	
2	390	Urea	
3	390	Urea	130	...	
4	390	Urea	130	130	
5	390	Urea	...	130	
6	Covercrop
7	195	Urea	Sulfur
	195	Manure	390+	390+	Covercrop
8	390	Urea	130	...	Covercrop
9	390	Urea	130	130	Covercrop
10	390	Urea	130	390	Covercrop
11	390	Urea	...	130	Covercrop
12	130	Dried blood	
	130	(NH ₄) ₂ SO ₄	Covercrop
	130	NaNO ₃	
13	390	Mixed fertilizers	390	390	Covercrop
14	195	Urea	390+	390+	Covercrop
	195	Manure	
15	390	(NH ₄) ₂ SO ₄	Covercrop
15a	390	(NH ₄) ₂ SO ₄	Covercrop. Lime since 1946
16	390	(NH ₄) ₂ SO ₄	Covercrop. Lime since 1927
17	390	Dried blood	Covercrop
18	390	Urea	Covercrop
19	260	Urea	
	260	Manure	Covercrop
20	390	Ca(NO ₃) ₂	
21	390	Ca(NO ₃) ₂	Covercrop
22	390	(NH ₄) ₂ SO ₄	
22a	390	(NH ₄) ₂ SO ₄	Lime since 1946
23	650	Ca(NO ₃) ₂	Covercrop
24	390	Ca(NO ₃) ₂	Sulfur, covercrop
25	325	Urea	Covercrop
	325	Manure	
26	390	NaNO ₃	
26a	390	NaNO ₃	Gypsum since 1946
27	390	NaNO ₃	Covercrop
27a	390	NaNO ₃	Covercrop. Gypsum since 1946
28	390	NaNO ₃	Covercrop. Gypsum since 1927
29	65	Urea	
	65	Manure	Covercrop
30	390	Manure in fall	
31	390	Manure in fall	Covercrop
32	390	Manure in spring	
33	390	Urea	Covercrop. No zinc sprays*
34	195	Urea	
	195	Manure	Gypsum, covercrop
35	195	Urea	
	195	Manure	Limestone, covercrop

* No zinc deficiency, probably because of spray drift from near-by plots.

TABLE 1—Continued

Treatment number	Nitrogen		Phosphorus, lbs P ₂ O ₅ /A	Potassium, lbs K ₂ /A	Amendments and/or covercrop
	lbs N/A	Source			
36.....	390	Urea	Alfalfa hay,† covercrop
37.....	390	Urea	Bean straw,† covercrop
38.....	390	Urea	Cereal straw‡
39.....	390	Urea	Cereal straw‡
40.....	325	Urea	
	65	Manure	Covercrop
41.....	130	Urea	
	130	Manure	Covercrop
42.....	195	Urea	
	195	Manure	Covercrop
43.....	390	Cottonseed meal	Covercrop
Continuity.....	195	Urea§	
	195	Manure	Covercrop

† Organic material added in amounts equivalent to that in treatment 40.

‡ Organic material added in amounts equivalent to that in treatment 42.

§ Changed to Ca(NO₃)₂ in the spring of 1948.

orange trees with guard rows of Valencia orange trees alternating in the same row with Marsh grapefruit trees. Four plots were assigned to each of 43 treatments and 25 plots were assigned to one treatment. This latter treatment is called the "continuity treatment" and has been used as a basis for estimating local variations in yields in the experimental area.

During the period 1927 to 1939 the rate of application of N in most treatments was one pound per tree per year, or about 130 pounds per acre per year in the cultivated and fertilized areas of the plots. There were approximately 90.75 trees per acre and about seven tenths of the area in the plots was in the cultivated and fertilized middles. In the winter of 1939-40 the basic rate of application of N was increased to three pounds per tree per year or about 390 pounds per acre per year. The lower rate of application was used to compare different sources of N, and the higher rate was used to completely eliminate available N as a factor and thus measure responses to other elements and to measure the secondary effects of various fertilizers in a shorter period of time.

Starting in 1934, the trees in all plots have been treated with zinc sprays to eliminate zinc deficiencies. After correction of the zinc deficiency, mild temporary symptoms of manganese deficiency have appeared but have been of no practical importance.

Previous to 1942 the irrigation interval was approximately four weeks. There was evidence that this interval was too long and thus the interval was reduced to three weeks. The more frequent irrigation increased yields in cases where poor water penetration had resulted from structural deterioration of the surface soil.

Parker and Batchelor (1942) reported the effects of fertilizers on yield of fruit for the first twelve years of the experiment, and Parker and Jones (1951) reported yield data for the period 1940-49 as well as a summary for the previous years. Aldrich, Parker, and Chapman (1945) reported the

effects of several nitrogenous fertilizers and soil amendments on the properties of the soil. Soil samples for this work were taken in 1943. Parker and Jenny (1945) reported studies on water infiltration and related soil properties as affected by cultivation and fertilization with organic materials. More recently several technical journal articles have reported various aspects of the effects of fertilizers and soil amendments on soil characteristics in this experiment (Pratt, Jones, and Chapman, 1956; Pratt, 1957; Pratt, Goulben, and Harding, 1957; Pratt and Goulben, 1957; Harding, Pratt, and Jones, 1958; Pratt and Harding, 1957).

Treatments. Table 1 presents the treatments that were used for the period 1939-40 until 1955 when the soil samples were taken. The treatments in the 1927 to 1939 period were essentially the same as in table 1 except that most of the treatments were 130 pounds N per acre per year. The treatments fit into a few main categories: (1) various sources of N with and without covercrops; (2) urea as a source of N with and without P and K and covercrops; (3) a series of treatments involving urea, manure, and other organic materials; (4) $(\text{NH}_4)_2\text{SO}_4$ with and without lime and NaNO_3 , with and without gypsum; and (5) various rates of N fertilization.

The source of phosphate was triple superphosphate. The source of potassium was K_2SO_4 for treatments 4, 5, 9, 10, 11, and KCl for treatments 7 and 14.

Soil and Soil Samples. The soil is a Ramona sandy loam derived from granitic alluvium. The surface soil had a pH of 6.8 in 1918 and was free of lime to about 24 inches in depth. The cation-exchange capacity varies from about 4.5 to 10 me per 100 g. The organic carbon content of the surface soil (0 to 12 inches) was about 0.4 per cent at the beginning of the experiment. There is little if any horizon of clay accumulation, but at variable depths of 40 to 60 inches there is a semihardpan consisting of granitic sand containing sufficient clay to bind the sand into a dense mass.

Soil samples taken in 1918, 1927, and 1955 were used in this study. The 1918 and 1927 samples were taken from the 0 to 12, 12 to 24, 24 to 36, and 36 to 48-inch depths, whereas the 1955 samples were taken from the 0 to 6, 6 to 12, 12 to 24, 24 to 36, and 36 to 48-inch depths. In most cases only the samples taken in 1927 from the 25 "continuity plots" were used to obtain the status of the soil before differential treatment was started. In other cases both the 1918 and 1927 samples were compared with samples taken in 1955. The 1955 samples were taken from the edge of the irrigated middles at a point about 18 inches from the drip of the trees. The samples from the 0 to 6- and 6 to 12-inch depths were composites of 32 cores and those from the other depths were composites of 16 cores. The samples were air-dried, ground to pass an 8-mesh screen, and were stored in paper containers. The samples collected in 1918 and 1927 had been stored in metal cans and had not been ground. These were ground and treated the same as the 1955 samples.

The pH at 1:1 dilution with water was determined for all soil samples taken in 1955. All other chemical analyses were limited to samples from certain treatments and the group of treatments taken for each set of analyses was not necessarily the same as that taken for other analyses. All chemical procedures used in analyzing the soil samples are described at the beginning of each section of the results.

Water. The average composition of the water was in me per liter: Ca, 2.43; Mg, 0.76; Na, 1.46; Cl, 0.63; SO_4 , 1.03; and HCO_3 , 3.00. There have been only minor variations from this composition during the years of the experiment. The water is of excellent quality for irrigation with a conductance of about 570 micromhos per cm, and a sodium content of 31 per cent. The water contains no residual Na_2CO_3 because the sum of Ca plus Mg is greater than the HCO_3 . The possible Na percentage, assuming that all the HCO_3 reacts with Ca and Mg, is 88 per cent.

TABLE 2
THE pH VALUE OF SOIL SAMPLES TAKEN IN 1918, 1927, AND
1955 FROM THE INDICATED DEPTHS

Treatment		Depth, inches				
Number	Description	0-6	6-12	12-24	24-36	36-48
	1918.....	6.8	(0-12)	6.9	7.2	7.4
	1927.....	7.6	(0-12)	7.5	7.4	7.7
	1955.....
1 and 6	Check.....	8.0	8.0	8.0	8.2	8.3
2 and 18	Urea.....	7.0	7.6	7.9	8.1	8.2
5 and 11	Urea, potash.....	7.1	7.5	7.8	8.0	8.0
3 and 8	Urea, phosphate.....	6.6	7.3	7.7	8.1	8.2
4 and 9	Urea, phosphate, potash.....	6.5	7.2	7.7	8.0	8.2
15 and 22	$(\text{NH}_4)_2\text{SO}_4$	4.0	3.9	4.5	7.2	7.5
15a and 22a	$(\text{NH}_4)_2\text{SO}_4$, lime since 1946.....	7.1	6.2	5.2	7.3	7.7
16	$(\text{NH}_4)_2\text{SO}_4$, lime since 1927.....	7.6	7.7	7.8	7.6	7.7
26	NaNO_3	8.5	8.7	8.8	8.5	8.4
27	NaNO_3 , covercrop.....	7.9	8.2	8.6	8.4	8.5
26a and 27a	NaNO_3 , gypsum since 1946.....	7.6	7.8	7.7	7.8	8.0
28	NaNO_3 , gypsum since 1927.....	7.6	7.8	7.6	7.7	7.8
20 and 21	$\text{Ca}(\text{NO}_3)_2$	7.7	7.9	7.9	8.0	8.0
30 and 31	Manure.....	7.7	7.8	7.9	8.0	8.0
	L.S.D. (5%).....	0.2	0.2	0.2	0.2	0.2

RESULTS

Acidity, Alkalinity, and Lime Accumulation. Table 2 presents data for the pH values of soil samples taken in 1918, 1927, and 1955. The pH values were measured with a Beckman Model H-2 meter using a 1:1 dilution with water. Covercrops had no effect on pH of the soil except in combination with NaNO_3 . With this N source the covercrop significantly reduced the pH in the soil of the 0 to 24-inch depth but had no effect on depths below 24 inches. As will be shown later, covercrops with NaNO_3 reduced the per cent soluble Na in the saturation extract compared to NaNO_3 alone.

Irrigation alone increased the pH significantly during the ten years prior to 1927 when differential treatment was started. In the check plots where irrigation water was the only material added the pH continued to increase to 8.0 in 1955.

Urea had a slight acidifying effect in the surface soil but had no such effect in the depths below 6 inches. Triple superphosphate had an acidifying effect that reduced the pH, in comparison to urea alone, about one-half unit in both the 0 to 6- and 6 to 12-inch depths. Potash had no effect.

The $(\text{NH}_4)_2\text{SO}_4$ produced a rapid acidification of the soil. Aldrich (1945) reported that by 1943 the surface soil in the plots treated with this source was pH 4.0. Lime added beginning in 1946 has been sufficient to bring the pH values back to near neutrality except in the 12 to 24-inch depth. The quantity of lime added in this treatment was one ton per acre per year after an initial application of two tons per acre or an accumulated total of 11 tons at time of sampling in 1955. Where lime was added throughout the experiment, the rate was four tons per acre every four years or an accumulated total of 28 tons per acre. This has been more than sufficient lime to prevent acidification of the soil. The pH in this treatment has increased slightly since 1927. The quantity of lime added in treatment 16 $(\text{NH}_4)_2\text{SO}_4$ plus lime

TABLE 3
INCREASE IN LIME IN THE SOIL OF FIVE TREATMENTS. THE
VALUES FOR 1918 SUBTRACTED FROM VALUES IN 1955

Treatment		Increase in lime at indicated depths (inches)				
Number	Description	0-6	6-12	12-24	24-36	36-48
		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1	Check.....	0.15	0.02	0.04	0.06	0.00
2	Urea.....	0.02	0.03	0.10	0.11	0.09
21	$\text{Ca}(\text{NO}_3)_2$	0.07	0.04	0.08	0.21	0.02
27	NaNO_3	0.10	0.08	0.14	0.11	0.03
31	Manure.....	0.24	0.01	0.05	0.08	0.05
	Average.....	0.12	0.04	0.08	0.11	0.04

since 1927) was 56,000 pounds per acre. Corrections for purity reduce this value to 53,200 pounds. The quantity of lime in the surface 6 inches in 1955 was 1.75 per cent or, assuming a weight of 2,000,000 pounds soil per acre 6 inches, 35,000 pounds per acre. There was no evidence of penetration of lime beyond the surface 6 inches and thus the difference, 18,200 pounds, is an estimate of the amount of lime neutralized by acidity from the $(\text{NH}_4)_2\text{SO}_4$. The amount of acidity from the $(\text{NH}_4)_2\text{SO}_4$, using data from Russell and Russell (1950) for calculations, was equivalent to 42,000 pounds of lime. The difference in potential acidity from the $(\text{NH}_4)_2\text{SO}_4$ and the amount of lime neutralized is equivalent to 23,800 pounds of lime. The alkalinity most likely to have neutralized this acid is that of the irrigation water, which contained 3.00 me. HCO_3 per liter. If all the HCO_3 in the water added were to have neutralized acidity developed from the $(\text{NH}_4)_2\text{SO}_4$, 58.5 acre feet of water would have been sufficient to provide the equivalent of 23,800 pounds of CaCO_3 . Unpublished information on water application and runoff from these plots would suggest that greater than 60 acre feet of water has penetrated the soil in this treatment.

Treatment with NaNO_3 alone increased the pH to 8.5 and above. Covercrops with NaNO_3 partially reduced this undesirable effect. Gypsum added since 1927, or since 1946, maintained or reduced the pH values to the same as those for the $\text{Ca}(\text{NO}_3)_2$ and manure treatments.

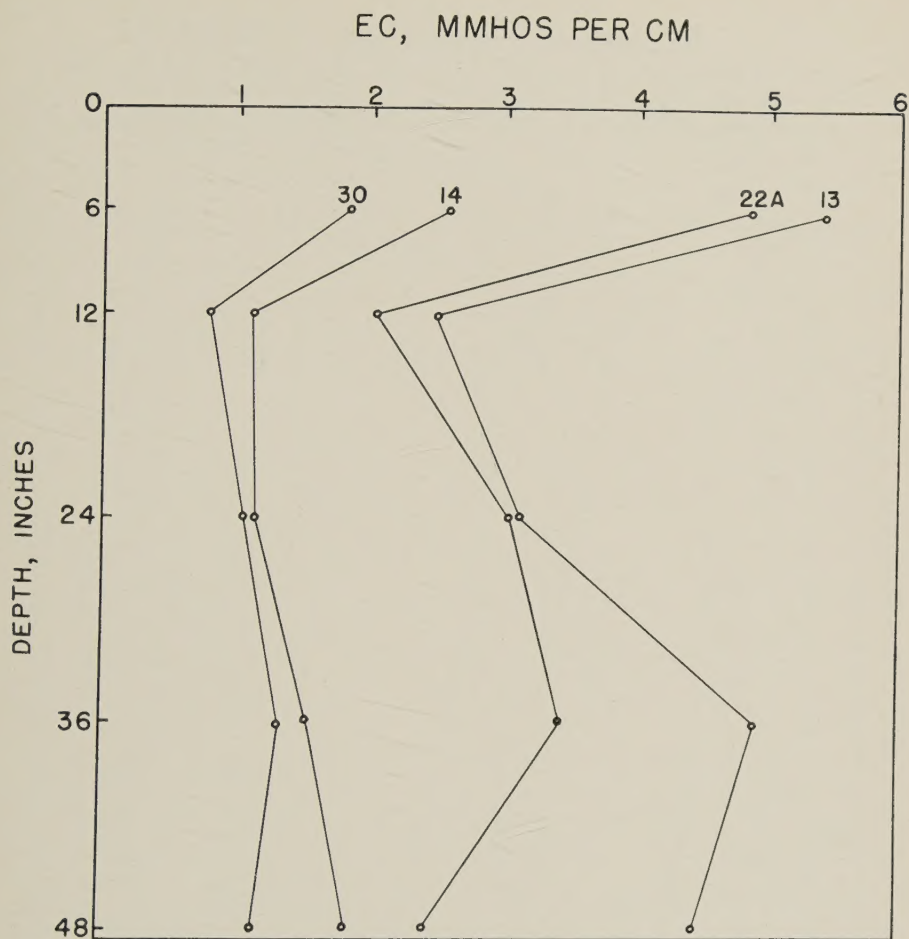


Fig. 1. Relation between depth in the soil and the conductivity of the saturation extract for four treatments. Treatments are: 30, manure; 14, urea, manure, phosphate, and potash; 22A, NH_4SO_4 plus lime since 1946; and 13, (8-8-8) mixed fertilizer.

Data for the increase in lime content of the soil during the period 1918 to 1955 are presented in table 3. In all of the five treatments except the urea treatment there was more lime accumulation in the 0 to 6-inch depth than in the 6 to 12-inch depth. In the urea treatment the slight acidification in the surface 6 inches probably produced this exception. Four of the five treatments showed that another point of maximum accumulation of lime was in the 24 to 36-inch depth. The exception to this was the NaNO_3 treatment where it was in the 12 to 24-inch depth. The total amount of lime accumulation was about the same in all treatments and was apparently independent of the amount of Ca added. Thus, the amount of accumulation was probably dependent on the HCO_3 added in the irrigation water.

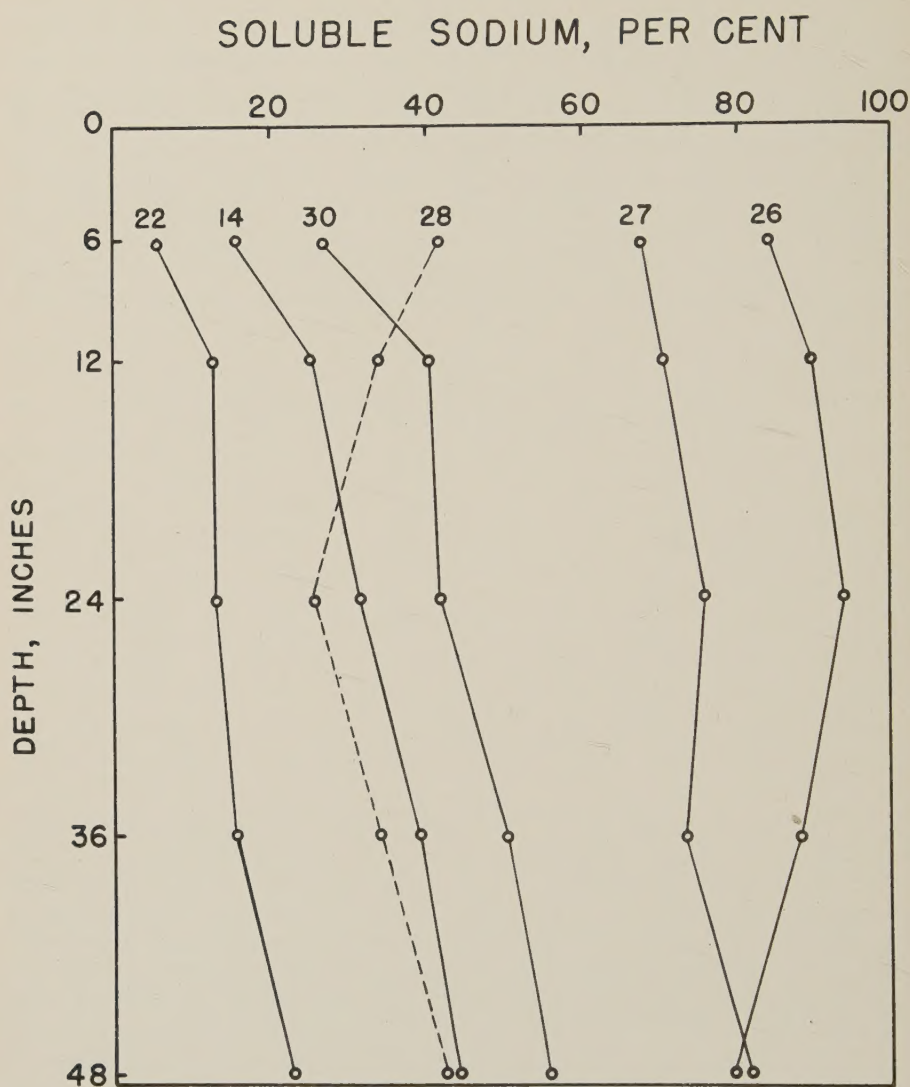


Fig. 2. Relation between depth in the soil and the soluble Na percentage of the saturation extract for six treatments. Treatments are: 22, $(\text{NH}_4)_2\text{SO}_4$; 14, urea, manure, phosphate, and potash; 30, manure; 28, NaNO_3 plus gypsum; 27, NaNO_3 and cover crops; 26, NaNO_3 .

TABLE 4

THE CONDUCTIVITY AND SOLUBLE SODIUM PERCENTAGE OF THE SATURATION EXTRACT OF THE SAMPLES OF THE 12-36-INCH DEPTH OF SOIL IN 1918, 1927, AND IN SAMPLES OF THE SAME DEPTH IN 1955 FROM VARIOUS TREATMENTS

Treatment		ECe at 25° C	Soluble sodium
Number	Description		
		<i>mmhos/cm</i>	<i>per cent</i>
1918	Before irrigation.....	0.61	24
1927	Before fertilization.....	1.34	38
1	Check.....	0.85	54
2	Urea.....	1.34	51
18	Urea, c.c.....	1.05	42
4	Urea, P ₂ O ₅ , K ₂ O.....	1.51	49
8	Urea, P ₂ O ₅ , c.c.....	1.01	39
10	Urea, P ₂ O ₅ , K ₂ O, c.c.....	1.92	30
11	Urea, K ₂ O, c.c.....	1.36	39
12	Mixed N sources, c.c.....	2.86	54
13	Mixed fertilizers (8-8-8), c.c.....	4.01	41
7	Urea, manure, P ₂ O ₅ , K ₂ O, S, c.c.....	1.40	30
14	Urea, manure, P ₂ O ₅ , K ₂ O, c.c.....	1.28	35
15	(NH ₄) ₂ SO ₄ , c.c.....	3.40	13
22	(NH ₄) ₂ SO ₄	5.61	26
22a	(NH ₄) ₂ SO ₄ , lime since 1946.....	3.25	15
20	Ca(NO ₃) ₂	1.30	42
21	Ca(NO ₃) ₂ , c.c.....	0.78	36
23	Ca(NO ₃) ₂ , split application, c.c.....	1.49	37
24	Ca(NO ₃) ₂ , S, c.c.....	2.07	18
26	NaNO ₃	5.10	91
26a	NaNO ₃ , CaSO ₄ since 1946.....	5.40	40
27	NaNO ₃ , c.c.....	4.09	75
28	NaNO ₃ , CaSO ₄ since 1927.....	3.72	30
30	Manure.....	1.17	45
31	Manure, c.c.....	0.80	41
34	Manure, c.c., CaSO ₄ , urea.....	2.52	17
35	Urea, manure, lime, c.c.....	1.03	51
17	Dried blood, c.c.....	1.35	49
42	Urea, manure, c.c.....	1.67	45
43	Cottonseed meal, c.c.....	1.14	45

Salinity. The electrical conductivity and concentration of various ions in the saturation extract were used for appraising salinity changes. Sodium, K, and Ca in the saturation extract were determined using a Perkin-Elmer Model 52-A flame photometer with Li as an internal standard. The remaining analyses and method of obtaining the saturation extract were determined by methods described in United States Department of Agriculture Handbook No. 60 (1954). The nitrate-N contents of the soil samples were calculated from the nitrate in the saturation extract.

The relation between the electrical conductivity of the saturation extract and depth of soil for four treatments is presented in figure 1. The relation in case of treatments 30 and 14 is typical of treatments with low salinity, and treatments 22a and 13 are typical of treatments with medium to high salinity. In all cases the lowest conductivity was in the 6 to 12-inch depth

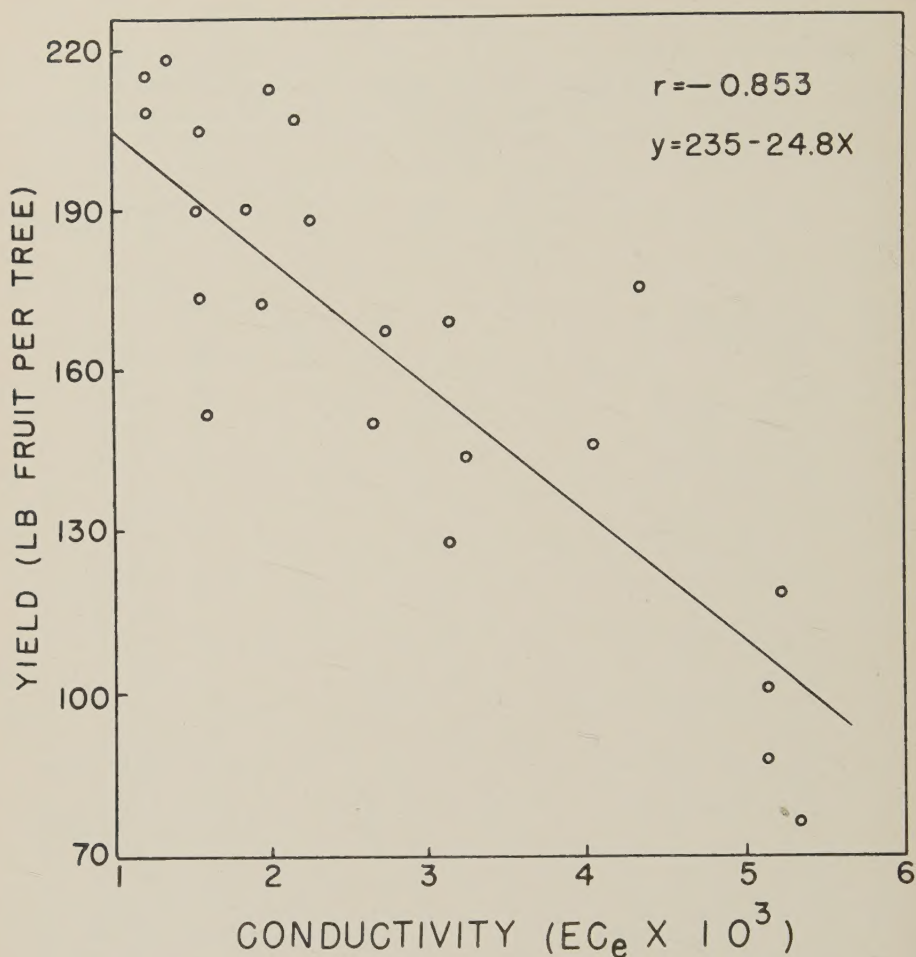


Fig. 3. Relationship between average conductivity of saturation extracts of soils, 0-48 inches, and average yield of orange fruits, 1951-1956 inclusive.

with much larger conductivities in the 0 to 6-inch depth and also with a general increase in conductivity with increase in depth below the 12-inch level. There was only a slight tendency toward an interaction between depth and treatment. Those treatments that produced low salinity had low salinity at all depths and those that produced high salinity had high salinity at all depths. Because of this, the average conductivity in the 12 to 36-inch depth was taken as a single valued index to the salinity in the soil.

The relation between depth in the soil and the soluble Na percentage of the saturation extract for six treatments is presented in figure 2. With treatments 22, 14, and 30, which are typical of all treatments except where NaNO_3 or NaNO_3 plus gypsum were added, there was a general increase in the

soluble Na percentage with increase in depth. With the NaNO_3 alone there was a maximum in the 12 to 24-inch depth whereas with NaNO_3 plus gypsum there was a minimum at this depth. Covercrops along with NaNO_3 reduced the soluble Na percentage about 15 per cent except in the 36 to 48-inch depth.

As with the conductivity of the saturation extract, the soluble Na percentage in the 12 to 36-inch depth was used as a single valued index of the accumulation of soluble Na in the soil.

The conductivity and soluble Na percentage of the saturation extract of the soil from the 12 to 36-inch depth in 1918 and 1927, and from 29 treatments in 1955, are presented in table 4. In the plots that received only irrigation water there was a consistent increase in soluble Na percentage with increase in years of irrigation. However, the 1955 samples of the check plots showed a lower conductivity than the samples taken in 1927.

The effect of cover crops was to reduce the conductivity and the soluble Na percentage as compared to the same treatments without covercrops. Applications of S increased the total salt concentration but reduced the soluble Na percentage. This effect of S was probably a result of increased Ca in solution from the action of H_2SO_4 on lime in the soil. Treatment with gypsum had the same effect as S on both the conductivity and the soluble Na percentage.

In all cases where salinity is high the fertilizer treatments are known to have reduced water penetration as a result of structural deterioration. Treatments with $(\text{NH}_4)_2\text{SO}_4$ or NaNO_3 have resulted in considerable salinity. Aldrich, Parker, and Chapman (1945) found that the surface samples from these treatments had lower macropore space, water-stable aggregation, and laboratory permeability than samples from the $\text{Ca}(\text{NO}_3)_2$, manure, or urea treatments. Recent studies have shown that the amount of water entering the soil (water added minus runoff) has been much lower in these plots than in those of the calcium nitrate or manure plots. Lime added to the $(\text{NH}_4)_2\text{SO}_4$ -treated plots, and gypsum added to the NaNO_3 -treated plots were effective in reducing both the conductivity and the soluble Na percentage.

Treatments 12 and 13 have produced relatively high salinity. Both of these treatments have acidified the soil to between pH 5 and 6 in the surface 6 inches.

The relationship between yield of orange fruits during 1951-56 and the average conductivity of the saturation extract of the soil in 1955 is presented in figure 3. The correlation coefficient was (-0.853) which is significant at the 0.001 per cent level. On the basis of this information, 73 per cent of the variance in yield is attributed to variance in soil salinity or closely associated factors such as available moisture.

In this experiment it is not possible to isolate the effect of salinity from that of low moisture availability. Where the fertilizer treatments have produced a deterioration of the soil structure with a resultant decrease in permeability to water, increased salinity has probably been associated with low moisture availability. Where water penetration has been more rapid as in the plots treated with $\text{Ca}(\text{NO}_3)_2$, or manure, salinity has remained low as a result of more water moving through the soil.

Organic Carbon and Nitrogen. Organic C was determined by a modification of the method of Walkley and Black (1934). The total N was determined by a Kjeldahl method. The $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ were subtracted from the total N to obtain organic N.

The data for the organic C and N in the 1927 samples from 12 continuity plots showed that the field was uniform in C and N at the beginning of differential fertilization. The average values for C for the 0 to 12; 12 to 24;

TABLE 5
ORGANIC C AND N AND C:N RATIO IN THE 0 TO 6 INCHES OF
SOIL IN THE PLOTS OF 20 TREATMENTS

Treatment*		C	N	C:N ratio
Number	Description			
		<i>per cent</i>	<i>per cent</i>	
1	None (check).....	0.40	0.048	8.3
6	Covercrop.....	0.46	0.056	8.3
2	Urea.....	0.42	0.050	8.3
18	Urea, covercrop.....	0.44	0.058	7.6
3	Urea, phosphate.....	0.43	0.050	8.6
8	Urea, phosphate, covercrop.....	0.48	0.059	8.2
22	$(\text{NH}_4)_2\text{SO}_4$	0.50	0.060	8.3
15	$(\text{NH}_4)_2\text{SO}_4$, covercrop.....	0.54	0.067	8.1
20	$\text{Ca}(\text{NO}_3)_2$	0.49	0.050	9.6
21	$\text{Ca}(\text{NO}_3)_2$, covercrop.....	0.55	0.057	9.7
36	Urea, alfalfa hay, covercrop†.....	0.49	0.067	7.4
37	Urea, bean straw, covercrop†.....	0.54	0.067	8.1
38	Urea, cereal straw, covercrop†.....	0.54	0.065	8.1
39	Urea, cereal straw, covercrop†.....	0.52	0.073	7.2
40	2.5 lbs N from urea, 0.5 lb N from manure, covercrop.....	0.69	0.086	8.0
41	1.0 lb N from urea, 1.0 lb N from manure, covercrop.....	0.90	0.105	8.6
42	1.5 lbs N from urea, 1.5 lbs N from manure, covercrop.....	1.01	0.118	8.7
19	2.0 lbs N from urea, 2.0 lbs N from manure, covercrop.....	1.11	0.142	7.8
25	2.5 lbs N from urea, 2.5 lbs N from manure, covercrop.....	1.22	0.140	8.7
31	3.0 lbs N from manure, covercrop.....	1.32	0.150	8.8
	L.S.D. (5%) for treatment means.....	0.06	0.008	0.8

* All nitrogen sources, except where indicated, were added at a rate of 130 lbs N per acre per year from 1927 to 1939, and 390 lbs per acre per year from 1939 to 1955.

† Organic material equivalent to dry weight of manure in treatment 40.

‡ Organic material equivalent to dry weight of manure in treatment 42.

and 24 to 36-inch depths were 0.283, 0.147, and 0.102 per cent, respectively, with standard errors of 0.008, 0.005, and 0.003 per cent. The average values for N for the respective depths were 0.0388, 0.0253, and 0.0203 per cent, with standard errors of 0.0012, 0.0008, and 0.006 per cent.

The organic C and N contents of the soil of the check plots in 1955 were not significantly different from the values for the field in 1927. Thus, under a system of management that included no fertilizers, organic materials, or covercrops, the organic matter of the soil was maintained at the original level.

All comparisons of the effects of the various treatments on the C and N contents of the soil were made by using the values for the 1955 samples of the check plots as a base. This was done because (a) the values for the

check plots in 1955 were essentially the same as those for the 1927 samples, and (b) the 1927 samples of the surface soil were taken from the 0 to 12-inch depth, whereas the surface samples in 1955 were taken from the 0 to 6-inch depth. Since soil samples gave no evidence of differences in effects of treatments at any depth below the surface 0 to 6 inches, only the data for that depth are presented.

The organic C and N and C:N ratio in the soil of the 0 to 6-inch depth for plots of 20 treatments are presented in table 5. The over-all effect of the covercrops was to increase the C and the N in the soil with no effect on the

TABLE 6

PHOSPHORUS SOLUBLE IN NaHCO_3 AND pH VALUES FOR THE SURFACE SOILS OF PLOTS HAVING RECEIVED NO PHOSPHATES OR ORGANIC MATERIALS. THE DATA ARE AVERAGES OF FOUR PLOTS EXCEPT FOR ALL $(\text{NH}_4)_2\text{SO}_4$ AND NaNO_3 TREATMENTS WHERE THEY ARE AVERAGES OF TWO PLOTS

Treat- ment number	Description	pH*	Soluble P, ppm
1	Check.....	8.1	6.6
6	Covercrop.....	8.0	5.5
20	Calcium nitrate.....	7.8	4.5
26	Sodium nitrate.....	8.5	5.7
26a	Sodium nitrate and gypsum since 1946.....	7.6	9.5
2	Urea.....	7.1	6.9
18	Urea and covercrop.....	7.0	5.7
24	Calcium nitrate, sulfur, and covercrop.....	5.8	19.7
22	Ammonium sulfate.....	4.0	30.6
22a	Ammonium sulfate and lime since 1946†.....	7.1	14.0
15	Ammonium sulfate and covercrop.....	4.1	31.6
15a	Ammonium sulfate, covercrop, and lime since 1946†.....	7.2	15.6
	L.S.D. (5%) for treatment means.....	0.1	2.0

* Averages were calculated from H ion concentrations.

† These plots were as acid as the $(\text{NH}_4)_2\text{SO}_4$ or $(\text{NH}_4)_2\text{SO}_4$ covercrop plots before liming started. The pH values were near 4.0 in 1943.

C:N ratio. The interaction between N source and covercrops was not significant, thus indicating that the effect of the covercrops was constant and independent of the fertilizer treatments. The average increase from the covercrops was 0.04 per cent C and 0.0078 per cent N.

The urea and urea-phosphate treatments had no effect on the organic C and N contents or on the C:N ratio. The $\text{Ca}(\text{NO}_3)_2$ treatment had no effect on the amount of organic N but did increase the organic C, with a resultant increase in the C:N ratio. The $(\text{NH}_4)_2\text{SO}_4$ treatment increased both the C and the N. One possible explanation for this effect is that the $(\text{NH}_4)_2\text{SO}_4$ plots became sufficiently acid so that there was a decrease in the rate of decomposition of the organic matter with a subsequent increase in the level of C and N.

The highest rate of application of manure increased the organic C and N values to about three times the values in 1927. The amount of N fertilizer added with manure had no apparent effect on the increase in C or N resulting

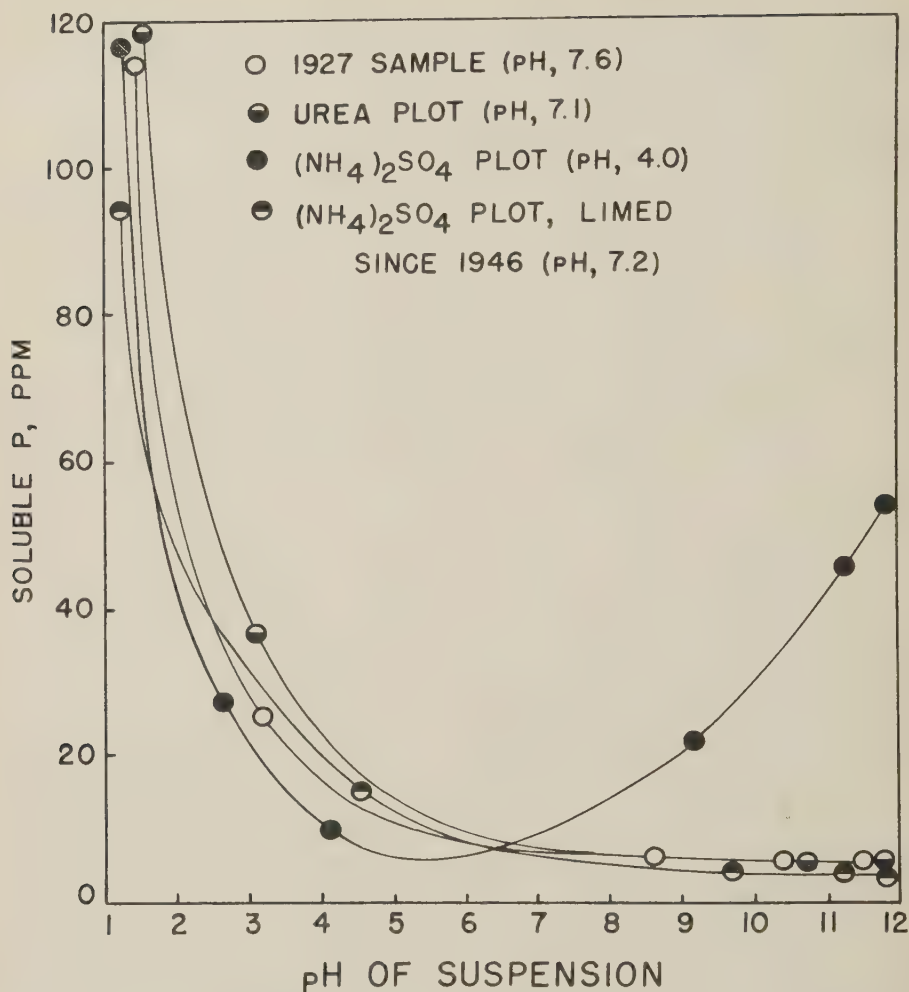


Fig. 4. Relation between soluble P and pH of soil suspended 0.1N HCl or 0.1 NaOH and various ratios of HCl to NaOH.

from the application of manure. The crop residues used plus adequate N were not so effective as an equivalent weight of manure in increasing the organic C content of the soil.

Phosphorus. Soluble P was measured by the method of Olsen *et al.* (1954), in which soil is extracted with 0.5 N NaHCO_3 at pH 8.5, using a 1:10 soil-to-solution ratio. In a few samples a determination was made of the P extracted by HCl-NaOH mixtures.

Samples for total P were ground to pass a 40-mesh screen. Total P was extracted from soils by the method of Shelton and Harper (1940), in which a 2-g sample of soil is digested with 4 ml of 72 per cent HClO_4 . The color-

imetric method used for the determination of P in the extracts was that of Dickman and Bray (1940) as modified by Mehta *et al.* (1954) to avoid interference by ferric iron. This procedure for extraction of total P from soils was checked against a Na_2CO_3 fusion procedure. The two procedures gave the same value within the limits of the error in the colorimetric method of the determination of P. Organic P was determined by use of the method of Mehta *et al.* (1954).

Samples from the surface 0 to 6 inches of soil from plots which had been variously treated but had received no phosphates or organic materials were used to measure the effect of soil reaction on the P soluble in NaHCO_3 . The soluble P and the pH of soils of 12 treatments are reported in table 6.

A highly significant correlation coefficient (-0.88) for the relationship between pH and soluble P indicates a significant increase in soluble P with increase in acidity. There was no tendency toward a maximum solubility at pH values near 6, as is expected and obtained with many soils. Obviously, there is no point in the acidification of this soil in which P is precipitated or adsorbed by the Fe, Al, or clay components of the soil faster than it is dissolved from the original basic forms.

The soluble P in the acid $(\text{NH}_4)_2\text{SO}_4$ plots was near 30 ppm. The limed $(\text{NH}_4)_2\text{SO}_4$ plots probably had an equally high soluble P previous to the application of lime in 1946. Thus, the lime treatment had the effect of reducing the soluble P. The soluble P in these limed plots was, however, more than twice that in the plots that received the urea treatment, where the pH was the same but the soils have not been acid. Therefore, the limed treatment had not reduced the soluble P to the value that it would have been had the soils not been acidified with $(\text{NH}_4)_2\text{SO}_4$. These data indicate that chemical changes that involve P when this soil is acidified are not completely reversible when the soil is limed.

The urea treatment reduced the pH of the soil slightly but did not increase the soluble P to any marked extent.

The NaNO_3 treatment increased the alkalinity of the soil. Half the plots in the NaNO_3 treatment were treated with gypsum from 1946 to 1955. The gypsum decreased the pH and produced a slight increase in soluble P.

Four soil samples were subjected to extraction with 0.1N HCl or 0.1N NaOH and mixtures of the two reagents by a procedure similar to those used by other investigators (Burd, 1948; Dean, 1938; Pratt *et al.*, 1955; Stelley and Pierre, 1943). A 3.5 g sample of soil was shaken for 30 minutes in 50 ml of solution. Part of the suspension was filtered, and the P in the filtrate was determined colorimetrically. The remainder of the suspension was used for a pH determination. The relationship between the soluble P and the pH of the soil suspensions is shown in figure 4.

The three 1955 samples used were from the surface 0 to 6 inches of soil; the fourth, or 1927 sample, was from the 0 to 12-inch soil depth. The data for the 1927 sample indicate that the P was dominantly in acid-soluble (probably apatite) forms, with no alkali-soluble P present. The data for the first 1955 sample, which was from a plot of the urea treatment, indicate that no changes resulted from this treatment. This sample also showed no alkali-soluble P. The second 1955 sample, the acid sample from an $(\text{NH}_4)_2\text{SO}_4$ -

treated plot, however, showed an accumulation of alkali-soluble P, although acid-soluble P was of the same order of magnitude as in the 1927 sample and in the sample from the urea treatment. These data indicate that in the acidification process some basic calcium phosphates were dissolved and converted to forms soluble in alkali. The third 1955 sample was from a plot that had been acid previous to 1946 and was limed back to pH 7.2. This soil can be considered to have developed alkali-soluble P in the same way as the soil of the $(\text{NH}_4)_2\text{SO}_4$ treatment. Thus the addition of lime reduced the alkali-soluble P back to the same values as for the nonacidified samples.

The similarity in the data for the acid soil that was limed back to pH 7.2 and the soils that had not been acidified indicates that the changes in

TABLE 7
ORGANIC PHOSPHORUS IN THE 0-12-INCH DEPTH IN 1927
AND FOR TWO TREATMENTS IN 1955. DATA ARE
AVERAGES OF FOUR PLOTS

Item	Treatment		
	1927	1955	
		Urea, covercrop	Manure*
Organic P, ppm.....	40	39	60
Organic P, per cent of total P.....	11	10	7

* Urea and manure both added at a rate of 3 lb N per tree per year since 1939, and 1 lb per tree per year previous to 1939.

forms of P compounds that took place with acidification and neutralization were reversible within the limits of the empirical method used to indicate these changes. The data for P soluble in NaHCO_3 , however, indicate that the changes were not completely reversible. The different results from the two methods of extraction can best be reconciled by the differences in the supposed action on the P compounds in the soil. The NaHCO_3 removes water-soluble P, a fraction of the surface P, and the phosphate that can be dissolved by the addition of the CO_3 ion which precipitates Ca ions and increases the solubility of some calcium phosphates. The NaOH solution, on the other hand, has no CO_3 ions to produce the dissolution of slightly soluble calcium phosphates, but has the effect of dissolving the phosphates of Fe and Al or removing phosphates from the clay-adsorbed forms. With this difference between the two reagents in mind, the data suggest that the NaOH-soluble forms have been completely changed to calcium phosphates by the addition of lime to the acid soil, but that some of these calcium phosphates are different compounds than the P compounds in the soil before it became acid.

The data for the quantities of organic P in the 0 to 12-inch depth of soil in 1927 and in plots of two treatments in 1955 are presented in table 7. The treatment with urea plus covercrop produced no significant change in organic P. The soil of the manure treatment showed an increase in organic P of about 50 per cent, as compared to the soil in 1927. However, as a result of a much

larger increase in inorganic P, the proportion of total P that was organic P was lower than in 1927. There were no detectable quantities of organic P in the soil below a depth of 12 inches.

Data for the change in P content of the soil in the irrigated middles of plots cropped with citrus for a 28-year period are presented in table 8. Average absorbed or removed by the trees was 8.5 per cent of the total P in the 0 to 36-inch depth of soil in the irrigated middles.

The loss of P from the soil, excluding loss by erosion and leaching, should be balanced for all practical purposes by a removal in harvested fruit plus deposition under the trees from leaf and fruit fall plus the amount in roots, trunk, and leaves of trees at time of soil sampling in 1955.

TABLE 8
PHOSPHORUS CONTENT OF THE 0-36-INCH DEPTH OF SOIL IN THE
IRRIGATED MIDDLES OF PLOTS IN 1927 AND 1955, AND THE
LOSS OF P DURING THE 28 YEARS OF CROPPING
WITH CITRUS

Treatment	1927	1955	Difference	L. S. D. at 5 per cent for difference	Difference as per cent of P in soil of irri- gated middles
	<i>ppm</i>	<i>ppm</i>	<i>ppm</i>	<i>ppm</i>	<i>per cent</i>
Check.....	398	363	35	21	8.8
Covercrop.....	366	341	25	14	6.8
Urea.....	435	393	42	20	9.7
Average.....	400	366	34	18	8.5

Data for the amounts of P accumulated from leaf fall in the surface foot of soil under the trees, removal in fruit, in the trees at time of sampling, and loss of P from the irrigated middles of plots of three treatments are presented in table 9. The accumulation of P under the trees was determined from samples taken from under the trees. The removal in the fruit was estimated from yield data and an average value for per cent P in the fruit. The amount in the trees at time of sampling was assumed to be the same as that of a 19-year-old grapefruit tree analyzed by Barnette *et al.* (1931). The total absorption by the trees was the same order of magnitude as the loss of P from the soil as estimated by soil analysis.

The removal of P in fruit was 1.4 per cent of the total P in the soil of the irrigated middles and 16 per cent of the P loss from the same soil area, whereas the P accumulated under the trees was 4.9 per cent of the P in the irrigated middles, and 58 per cent of the P loss. Thus, most of the P absorbed by the trees was returned to the soil and accumulated in the surface soil under the trees. The P accumulated in this manner is probably more available than the original P in the soil. The depletion of P from soils by removal in citrus fruits is essentially an extremely slow process and is one possible explanation of the fact that citrus orchards seldom develop P deficiencies.

All estimates of increases in soluble P and total P were obtained from comparisons among the 1955 samples of the plots of various treatments. The objective here was to find to what extent soluble phosphates had accumulated and penetrated into the lower depths of the soil, as well as to compare the effects of inorganic phosphates versus manure on the increase in P. The com-

TABLE 9
PHOSPHORUS ACCUMULATION UNDER TREES FROM LEAF FALL,
REMOVAL IN FRUIT, ESTIMATED IN TREES AT TIME OF
SAMPLING OF SOIL, AND LOSS OF P FROM IRRIGATED
MIDDLE (0-36-INCH DEPTH)

Treatment	Accumulation under trees	Removal in fruit	In trees	Total absorption by trees	Loss from soil
	lbs/A	lbs/A	lbs/A	lbs/A	lbs/A
Check.....	209	23	55	287	301
Urea.....	130	85	55	270	353
Covercrop.....	...	32	55	...	210
Average.....	165	47	55	278	288

TABLE 10
EFFECT OF PHOSPHATE ADDITIONS (IN THE FORM OF TREBLE
SUPERPHOSPHATE AT THE RATE OF 1 POUND P_2O_5 PER TREE
PER YEAR) ON $NaHCO_3$ -SOLUBLE P AND TOTAL P IN
CITRUS SOIL AT VARIOUS DEPTHS*

Soil depth	Soluble P				Total P			
	Phos- phated plots	Nonphos- phated plots	Difference	L.S.D. at 5 per cent difference	Phos- phated plots	Nonphos- phated plots	Difference	L.S.D. at 5 per cent difference
inches	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
0-6.....	44.2	6.3	37.9	5.9	902	357	545	59
6-12.....	23.9	2.2	21.7	4.0	464	304	160	46
12-24.....	12.9	1.8	11.1	4.0	434	358	76	65
24-36.....	5.4	2.8	2.6	1.9	462	422	40	57
36-48.....	3.0	2.2	0.8	1.1	486	434	52	81

* Data are averages of eight plots. Four of the eight phosphated plots received urea plus phosphate, and four received urea plus phosphate plus covercrop. Four of the eight nonphosphated plots received urea, and four received urea plus covercrop.

parison of 1955 samples with 1927 samples would have given a biased comparison in the lower horizons because it would not correct for decreases in P had there been no phosphates moving into these depths. The comparison of the 1955 samples of plots where P was added, with the 1955 samples of plots receiving no P, presents a more valid estimate of accumulation and movement into the soil.

Table 10 contains data for a comparison of eight plots that received treble superphosphate at a rate of one pound P_2O_5 per tree per year (129.5 pounds

per acre per year) and eight plots treated in identical manner except that no P was added. There have been significant increases in soluble P from the phosphate application down to and including the 24 to 36-inch depth. The data for total P indicate a significant increase in total P in the 0 to 6, 6 to 12, and 12 to 24-inch depths. The increase in total P in the soil of the 24 to 36-inch depth was significant at the 10 per cent probability level but not at the 5 per cent level.

More than 80 per cent of the accumulated P was in the 0 to 12-inch depth, and more than 60 per cent was in the 0 to 6-inch depth. Thus, the data presented here show that small amounts of the phosphates added to the surface

TABLE 11
EFFECT OF VARIOUS FERTILIZER TREATMENTS ON THE
CATION-EXCHANGE CAPACITY OF SOIL OVER A
PERIOD OF 28 YEARS (1927 TO 1955)

Treatment	Accumulated total K added*	Cation-exchange capacity		
		0-12 in	12-24 in	24-36 in
	lbs/A	me/100 g	me/100 g	me/100 g
Before fertilization†.....	0	4.9	6.6	6.6
Urea.....	0	4.7	6.4	6.6
Urea, phosphate.....	0	4.3	6.1	5.9
Urea, potash.....	3,000	4.3	6.2	6.0
Urea, phosphate, potash.....	6,700	4.7	6.1	6.5
Urea, manure, phosphate, potash.....	17,000	6.4	6.0	6.1
L.S.D. (5%) between treatment means.....	0.4	N.S.‡	N.S.‡

* 1927-1955.

† Samples taken in 1927.

‡ N.S.—not significant.

will move into the lower depths of the soil. These data agree with those of other investigators (Chapman, 1934; Robinson and Jones, 1927; Spencer, 1957; and Stephenson and Chapman, 1931).

The average increase in soluble P in the 0 to 6-inch depth of the manure plots was 69.2 ppm, when manure was added at a rate of three pounds of N per tree per year, and 27.4 ppm when manure was added at a rate of 1.5 pounds N per tree per year. The total quantity of P added in these manure treatments has not been determined; but the total quantity can be approximated on the assumption that the P_2O_5 content was half the N content. On this basis the calculated amounts added were 1,700 pounds P per acre and 850 pounds per acre, respectively, for the two treatments. These values can be compared with an application of 1,583 pounds P per acre in the plots that received treble superphosphate. The ratio of accumulated soluble P to total P added is 0.041, 0.032, and 0.024, respectively, for the manure at the higher rate, manure at the lower rate, and treble superphosphate.

Cation-exchange Capacity.—The cation-exchange capacity was measured by the method of Mehlich (1948), after an extraction with $N HCl$ to remove excess carbonates.

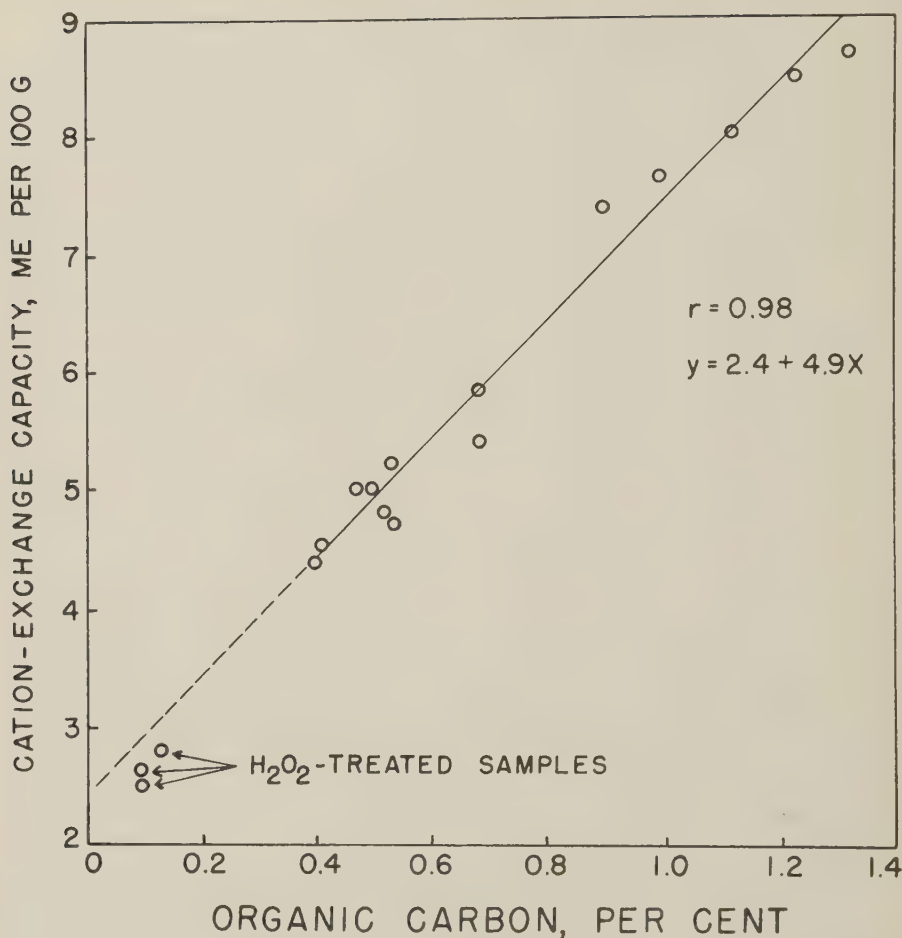


Fig. 5. Relation between cation-exchange capacity and organic C content of samples of the 0-6 inches of soil taken in 1955.

In 1927 the soil was relatively uniform in cation-exchange capacity. The range in values for six plots representing various areas in the field was less than 1 me/100 g for each of the following depths: 0 to 12, 12 to 24, and 24 to 36 inches.

Data for the cation-exchange capacity of the soil in 1927 and of samples of soil from plots of five treatments in 1955, and the total accumulated K added from 1927 to 1955, are presented in table 11. Cation-exchange capacity was not affected by urea, phosphate, and potassium applied individually or collectively. Only the treatment that included manure affected the exchange capacity and then only in the surface soil (0 to 6 inches). Where both manure and K salts were added, the total K added represents 21.8, 10.9, 5.4, and 3.6 me/100 g, if assumed to be distributed uniformly through depths

of 0 to 6, 0 to 12, 0 to 24, and 0 to 36 inches, respectively. In spite of the large quantity of K added in this treatment there was no reduction in cation-exchange capacity by K fixation.

The relation between cation-exchange capacity and organic C content of samples of the surface 0 to 6 inches of soil is presented in figure 5. This highly significant correlation between organic C and cation-exchange capacity indicates that the contribution of the mineral part of the soil to the cation-exchange capacity was nearly the same in all plots.

Extrapolation of the regression line (fig. 5) to zero per cent organic C indicates the cation-exchange capacity of the mineral part of the soil, assuming no interaction between the mineral and the organic matter, to be 2.4 me/100 g. To check this value, three samples containing 0.44, 0.64, and 1.07 per cent organic C, respectively, were subjected to an H_2O_2 -treatment, after which cation-exchange capacity and organic C were determined. Values for the H_2O_2 -treated samples are shown in figure 5 but were not used in the calculation of the regression equation. The values do, however, come close to the regression line and are only slightly higher than the Y intercept value of 2.4.

According to Broadbent (1953) the two disadvantages of the estimation of the cation-exchange capacity of the organic matter by the difference before and after H_2O_2 oxidation are that the oxidation of the organic matter is not complete and the H_2O_2 unmask some exchange sites which are blocked by interaction between organic matter and clay. With this soil the H_2O_2 treatment destroyed 85 per cent of the organic matter. Apparently, no exchange sites were unmasked, because the cation-exchange capacity values for the H_2O_2 -treated soil fell below rather than above the projected regression line. Thus, 46 to 71 per cent of the cation-exchange capacity of the surface soil is in the organic matter. This is probably typical of a large number of relatively sandy soils in California. Because of the small quantity of clay in the surface soil, the organic matter, even though it is present in small amounts, makes up half or more of the exchange capacity.

The increase in cation-exchange capacity with increase in organic C was 4.9 me/100 g per 1 per cent C. The calculated exchange capacity of the organic C is thus 490 me/100 g, which means that there is an average of 1 cation-exchange radical for each 17 atoms of organic C.

The data in figure 5 are from plots that received various types of organic residues, namely, manure, alfalfa hay, cereal straw, bean straw, and cottonseed meal. The cation-exchange capacity per gram of C in the organic matter was the same, irrespective of the type of organic materials added to the soil. Although the fact that the products of decomposition of the various organic materials had the same exchange capacity per gram of C is not proof that the products were identical, it is one indication of their similarity.

Exchange Acidity. The total exchange acidity was extracted from soil samples by leaching with 0.5N BaCl_2 . The displaced acidity was determined by a titration of the leachate, heated to about 90° C with a standard NaOH solution until the leachate retained the faint pink of the phenolphthalein end point. Exchangeable Al was extracted with 0.5N BaCl_2 and the Al determined colorimetrically by the method of Chenery (1948). Exchangeable

Mn was extracted using neutral NH_4OAc solution, and the Mn was determined colorimetrically.

Data for the total exchange acidity, exchangeable Al, and Mn, and pH values of soils from the $(\text{NH}_4)_2\text{SO}_4$ treatment are presented in table 12. The cation-exchange capacity for these samples was 4.8, 5.0, and 6.2 me/100 g for the 0 to 6, 6 to 12, and 12 to 24-inch depths, respectively, and thus the exchange acidity represented 33, 52, and 16 per cent, respectively.

The exchangeable or extractable Al was 40, 65, and 60 per cent of the total exchange acidity for the 0 to 6, 6 to 12, and 12 to 24-inch depths, respectively. Thus, exchangeable Al represented about half of the total exchange acidity in these acid samples.

TABLE 12
EXCHANGE ACIDITY, EXCHANGEABLE Al AND Mn, AND
THE pH OF SOILS TREATED WITH $(\text{NH}_4)_2\text{SO}_4^*$

Soil depth <i>inches</i>	pH	Milliequivalents per 100 g		
		Exchange acidity	Exchangeable	
			Al	Mn
0-6.....	4.0	1.5	0.6	0.03
6-12.....	3.9	2.6	1.7	0.07
12-24.....	4.4	1.0	0.6	0.16
24-36.....	7.2	0.01

* The $(\text{NH}_4)_2\text{SO}_4$ was added at the rate of 130 lbs N per acre per year from 1927 to 1938, inclusive, and at the rate of 390 lbs N per acre per year from 1939 to 1955 inclusive.

The exchange acidity in samples of all other treatments was so small that it was considered of no importance in the suite of exchangeable cations.

Exchangeable Ammonium. Exchangeable NH_4 was extracted from soils by a KCl solution and the extracted NH_4 determined by distillation into a standard acid. An estimate of fixed NH_4 was obtained by noting the difference between the quantity of NH_4 distilled from the soil when treated with 0.2N NaOH and that when treated with 0.2N KOH as suggested by Allison and Roller (1955).

The acid soils contained measurable amounts of exchangeable NH_4 , whereas the neutral soils contained only traces of NH_4 . The soil of the $(\text{NH}_4)_2\text{SO}_4$ treatment had 1.05, 0.27, and 0.04 me NH_4 per 100 g for the 0 to 6, 6 to 12, and 12 to 24-inch depth, respectively. The pH values for these depths were 4.0, 3.9, and 4.4, respectively. Soils treated with $(\text{NH}_4)_2\text{SO}_4$ and lime contained less than 0.04 me NH_4 per 100 g at all depths.

Fixed NH_4 was found in measurable quantities only in the surface soil of the $(\text{NH}_4)_2\text{SO}_4$ treated plots. In this soil the fixed NH_4 was 0.28 me per 100 g.

Exchangeable Sodium. Exchangeable Na was extracted using neutral normal NH_4OAc and the Na was determined flame photometrically. The water-soluble Na was subtracted from the Na in the NH_4OAc extract to obtain the data for exchangeable Na. Data for exchangeable Na for the sample

taken in 1927 and for samples taken in 1955 from plots of 17 treatments are presented in table 13.

In the comparisons of covercrop versus no covercrop there was less exchangeable Na in the 12 to 24 and 24 to 36-inch depths in the covercrop plots. The only exception to this was in the case of the $\text{Ca}(\text{NO}_3)_2$ treatment where there were no differences between covercrop and no covercrop. The maximum effect of the covercrops in reducing exchangeable Na was with the

TABLE 13
EXCHANGEABLE Na (NOT INCLUDING WATER-SOLUBLE) IN SOIL
SAMPLES TAKEN IN 1927 AND IN 1955. DATA ARE AVERAGES
OF THREE PLOTS EXCEPT TREATMENTS 22, 15, 22a, 26,
AND 26a, WHICH ARE AVERAGES OF TWO PLOTS

Treatment		Exchangeable Na at indicated depths, per cent of cation-exchange capacity			
Number	Description	0-6 in	6-12 in	12-24 in	24-36 in
	1927				
	Before fertilization.....	1.6 (0-12)	5.6	3.3
	1955				
1	Check.....	2.7	2.4	4.2	6.8
2	Urea.....	1.7	1.4	4.5	9.2
18	Urea, covercrop.....	1.7	2.2	3.5	7.0
4	Urea, phosphate, potash.....	0.4	1.4	4.4	10.8
11	Urea, phosphate, potash, covercrop.....	1.5	2.2	4.2	9.7
20	$\text{Ca}(\text{NO}_3)_2$	1.0	2.2	3.7	7.0
21	$\text{Ca}(\text{NO}_3)_2$, covercrop.....	1.7	2.2	3.5	7.0
22	$(\text{NH}_4)_2\text{SO}_4$	0.0	0.4	5.7	11.5
15	$(\text{NH}_4)_2\text{SO}_4$, covercrop.....	0.8	0.8	1.6	3.9
22a	$(\text{NH}_4)_2\text{SO}_4$, lime since 1946.....	1.2	0.8	1.8	3.0
30	Manure.....	1.0	1.2	2.7	6.2
31	Manure, covercrop.....	1.6	1.6	2.4	5.6
26	NaNO_3	12.0	25.6	49.0	50.0
27	NaNO_3 , covercrop.....	20.0	15.4	45.0	35.0
26a	NaNO_3 , CaSO_4 since 1946.....	4.6	5.4	16.5	15.8
28	NaNO_3 , CaSO_4 since 1927, covercrop.....	6.7	3.4	7.4	11.7
13	Mixed complete fertilizers, covercrop.....	2.7	2.4	7.9	15.6

$(\text{NH}_4)_2\text{SO}_4$ and NaNO_3 fertilizers. With $(\text{NH}_4)_2\text{SO}_4$ the covercrop was almost as effective in reducing exchangeable Na as was treatment with lime since 1946. In the 0 to 6-inch depth there was more exchangeable Na with than without covercrops. The only exception to this was with urea (Treatments 2 and 18) where there was the same amount in each treatment. The maximum effect of the covercrops in increasing exchangeable Na in the surface 6 inches was with NaNO_3 . The slightly higher exchangeable Na with the covercrop is probably a result of greater water loss from the surface 6 inches with the covercrop.

Exchangeable Calcium. Exchangeable Ca was calculated as the cation-exchange capacity minus the sum of exchange acidity and exchangeable Na, NH_4 , K, and Mg. Data for the exchangeable Ca for samples taken from four plots in 1927 and for samples taken in 1955 from plots of 11 treatments are

TABLE 14
EXCHANGEABLE Ca FOR SAMPLES TAKEN IN 1927 AND IN 1955
FROM PLOTS OF ELEVEN TREATMENTS

Treatment		Exchangeable Ca at indicated depths per cent of cation-exchange capacity			
Number	Description	0-6 in	6-12 in	12-24 in	24-36 in
	1927				
	Before fertilization.....	77 (0-12)	..	68	64
	1955				
1	Check.....	77	80	73	62
2	Urea.....	77	80	73	62
18	Urea, covercrop.....	79	76	74	62
20	Ca(NO ₃) ₂	85	82	77	70
22	(NH ₄) ₂ SO ₄	31	32	63	59
22a	(NH ₄) ₂ SO ₄ , lime since 1946.....	87	86	87	80
26	NaNO ₃	70	66	32	35
26a	NaNO ₃ , gypsum since 1946.....	85	84	74	77
28	NaNO ₃ , gypsum since 1927.....	83	86	85	79
30	Manure.....	71	64	68	65
10	Urea, manure, phosphate, potash, covercrop.....	67	66	71	71

TABLE 15
EXCHANGEABLE Mg AS CALCULATED FROM AN EXCHANGE
EQUATION AND AS DETERMINED BY CHEMICAL
METHODS FOR SOIL SAMPLES THAT
CONTAINED NO FREE
CARBONATES

Plot	Soil depth	Exchangeable Mg	
		Calculated	Determined
	<i>inches</i>	<i>me/100 g</i>	<i>me/100 g</i>
M-38.....	0-6	0.27	0.33
	6-12	0.41	0.36
I-18.....	0-6	0.28	0.20
	6-12	0.24	0.33
Average.....	0.30	0.31

presented in table 14. The data for treatments 2 and 18 are typical of most of the treatments not presented in table 14.

The exchangeable Ca was higher where Ca as Ca(NO₃)₂, lime, or gypsum was added as compared to all other treatments except in the surface 6 inches of soil in the manured plots where the exchangeable Ca was about 2 me per 100 g higher than in all other plots. The high exchangeable Ca in the manured plots is a result of the higher cation-exchange capacity that resulted from the increase in organic matter.

There was much less exchangeable Ca in the plots treated with (NH₄)₂SO₄ and in those treated with NaNO₃ than in all other plots.

TABLE 16
CALCULATED VALUES FOR EXCHANGEABLE Mg IN SOIL SAMPLES
TAKEN IN 1927 AND IN 1955, AND THE DECREASE IN
EXCHANGEABLE Mg DURING 28 YEARS OF
DIFFERENTIAL FERTILIZATION*

No.	Treatment Description†	Exchangeable Mg at given depth (inches)				Decrease in exchangeable Mg (0-36-in. depth)
		0-6	6-12	12-24	24-36	
		<i>me per 100 g</i>				<i>lbs/acre</i>
	1927					
	Before fertilization.....	1.01 (0-12)		1.89	1.97	
	1955					
1	Check.....	0.74	1.03	1.32	1.95	346
2	Urea.....	0.70	0.74	1.26	1.76	547
4	Urea, phosphate, potash.....	0.85	0.83	1.38	1.45	576
7	Urea, manure, phosphate, potash, sulfur, covercrop.....	1.20	0.91	1.24	1.28	604
13	Nitrogen, phosphate, potash from mixed fer- tilizers, covercrop.....	0.21	0.46	0.41	0.57	1699
20	Ca(NO ₃) ₂ , 290 lbs N per acre.....	0.42	0.61	0.95	1.46	936
23	Ca(NO ₃) ₂ , 650 lbs N per acre.....	0.40	0.51	0.61	0.78	1454
26	NaNO ₃	0.56	0.66	1.00	0.94	1110
26a	NaNO ₃ , CaSO ₄ from 1946 to 1955.....	0.27	0.32	0.36	0.82	1627
28	NaNO ₃ , CaSO ₄ from 1927 to 1955.....	0.27	0.31	0.33	0.49	1800
15	(NH ₄) ₂ SO ₄ , covercrop.....	0.37	0.30	0.98	1.56	950
22	(NH ₄) ₂ SO ₄	0.22	0.28	1.14	1.81	806
22a	(NH ₄) ₂ SO ₄ , CaCO ₃ from 1946 to 1955.....	0.39	0.50	0.54	0.97	1398
42	Urea, manure, covercrop.....	1.45	0.91	1.37	1.60	302
30	Manure.....	1.49	1.08	1.36	1.66	274
	L.S.D. 5 per cent.....	0.14	0.16	0.24	0.32	187

* Averages of 4 plots for 1927 samples; averages of 2 plots for samples from treatments 15, 22, 22a, 26, and 26a; averages of 3 plots for all others.

† In all treatments except 7, 23, and 42, the rate of application of N was 130 lbs per acre per year from 1927 to 1938 inclusive, and 390 lbs per acre per year from 1938 to 1955 inclusive. In treatments 7 and 42, the rate was 390 lbs N per acre per year from 1927 to 1955 inclusive; and in treatment 23 the rate was 130 lbs N per acre per year from 1927 to 1938 inclusive, and 650 lbs per acre per year from 1939 to 1955 inclusive.

The loss of exchangeable Ca with the acid (NH₄)₂SO₄-treated plots was mainly in the 0 to 6, 6 to 12, and 12 to 24-inch depth (the depths that were acidified), whereas with NaNO₃ the decrease in exchangeable Ca extended throughout the 0 to 36-inch depth and was greatest in the lower depths.

Exchangeable Magnesium. Exchangeable Mg was calculated by using a cation-exchange equation, as proposed by Reitemeier (1946), and McColloch *et al.* (1957). The equation used was the following:

$$\text{MgX} = \frac{(\text{DX}) (\text{Mg}^{++})}{(\text{Mg}^{++}) + 1.6 (\text{Ca}^{++})}$$

where DX = cation-exchange capacity minus sum of exchangeable Na, NH₄, K, and acidity, X = cation-exchange capacity, and Mg⁺⁺ and Ca⁺⁺ = concentration of the respective cation in milliequivalents per liter in the saturation extract. The use of the calculated values for Mg was necessary because of the

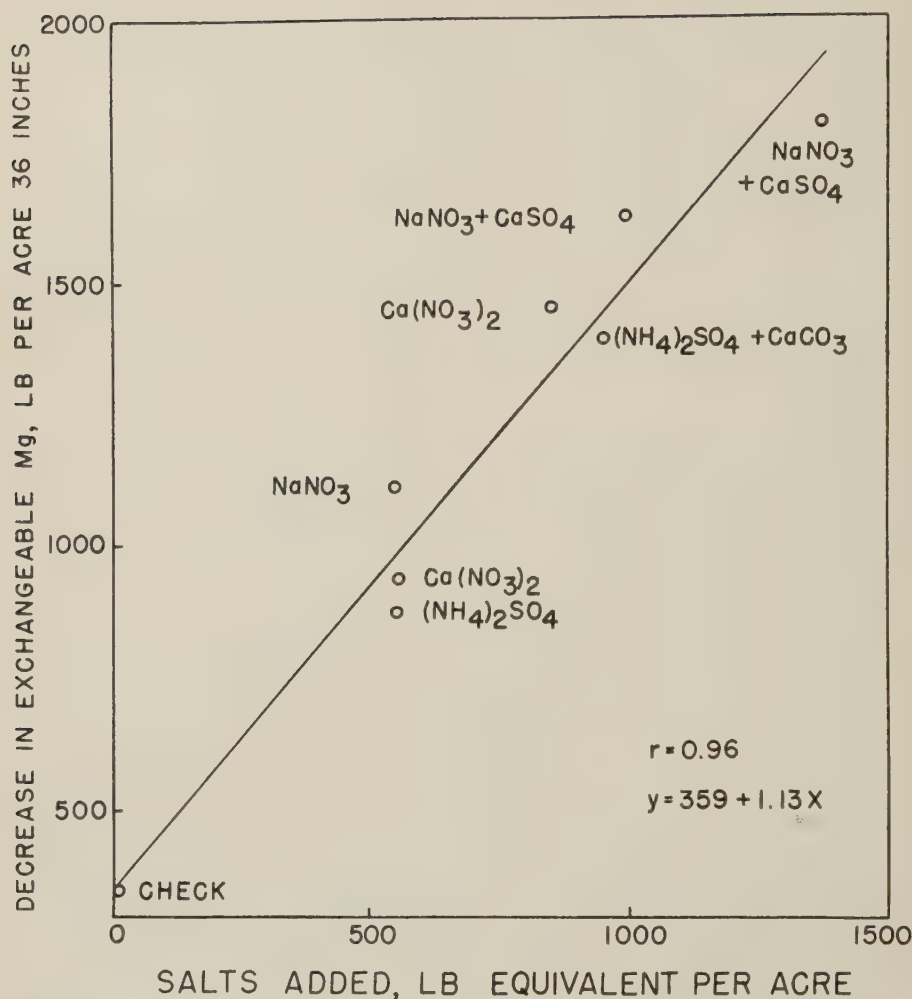


Fig. 6. Relation between the decrease in exchangeable Mg and the accumulated total salts added in fertilizers and soil amendments during 28 years of irrigation and fertilization.

presence in the soil samples of Mg carbonates which dissolve in NH_4OAc and most other extraction solutions. The exchangeable Mg was extracted with NH_4OAc and determined chemically for a few samples that were sufficiently acid that the Mg and Ca carbonates were not present. The Mg was precipitated and weighted as the quinolate salt.

Data for exchangeable Mg as calculated from an exchange equation and as determined by chemical methods for several soil samples that contained no free carbonates are presented in table 15. The calculated values and determined values are of the same order of magnitude. There are, however, large percentage errors for some of the samples. The error for the average

of the calculated values, considering the determined values to be the standard, is only 3.2 per cent. The agreement between the two methods is considered to be satisfactory in view of the fact that the calculated values contain accumulated errors from the determinations of exchangeable Na, K, NH_4 , acidity, cation-exchange capacity, and quantities of soluble Mg and Ca in the saturation extract.

Data for the calculated values of exchangeable Mg in samples taken in 1927 and in 1955, and for decrease in exchangeable Mg during 28 years of fertilization, are presented in table 16. The data suggest that the decrease in exchangeable Mg increased with increase in amounts of fertilizers and soil amendments added, except that the decrease in exchangeable Mg was less where manure was added than where an equivalent amount of N was added in mineral salts. The amount of Mg in the manure undoubtedly caused this effect. For 8 of the 15 treatments listed in table 16 the accumulated total quantities of mineral salts added as fertilizers and as soil amendments could be calculated accurately. Treatments 15 and 22 were considered as one treatment. Total salts were calculated in terms of pound-equivalents per acre. The relation between decrease in exchangeable Mg and the pound-equivalents of salt added during the 28 years of irrigation and fertilization is shown in figure 6. The decrease in exchangeable Mg was highly correlated with the pound-equivalents of salts added, in fact better than 92 per cent of the variance in decrease in exchangeable Mg was associated with variance in amount of salts added.

Treatments 7, 42, and 30 cannot be made to fit into the regression equation in figure 6 because manure was applied in each case. The K and P carriers for treatment 13 were K_2SO_4 and triple superphosphate, and one third of the N was supplied from each of $(\text{NH}_4)_2\text{SO}_4$, NaNO_3 , and dried blood. The calculated pound equivalents of salts added, neglecting the blood, was 865. Thus, the point for treatment 13 is above the regression line in figure 7. Treatments 2 and 4, where urea was the source of N, do not fit the regression line, perhaps because urea hydrolyzes to give an anion (CO_3) that is unstable. The decrease in exchangeable Mg was significantly lower in treatments 2 and 4, where urea was the source of N, than where $\text{Ca}(\text{NO}_3)_2$, $(\text{NH}_4)_2\text{SO}_4$, or NaNO_3 was the source of N.

The cation-exchange equation

$$\frac{\text{Mg}^{++} \text{CaX}}{\text{Ca}^{++} \text{MgX}} = 1.6$$

where Mg^{++} and Ca^{++} are the concentrations of these ions in the irrigation water and CaX and MgX are the amounts of these ions in me/100 g in the exchangeable form in the soil, was used to calculate the ratio of the exchangeable Mg to Ca that would be in equilibrium with the Mg and Ca in the irrigation water. The ratio was 0.20. The ratios of exchangeable Mg to Ca in the soil of the check plots that had received no treatment other than irrigation were 0.20, 0.28, 0.29, and 0.48, respectively, for soil at the 0 to 6, 6 to 12, 12 to 24, and 24 to 36-inch depths. Thus, the 0 to 6-inch depth of soil had reached equilibrium with the irrigation water, but the soil of the other depths had not.

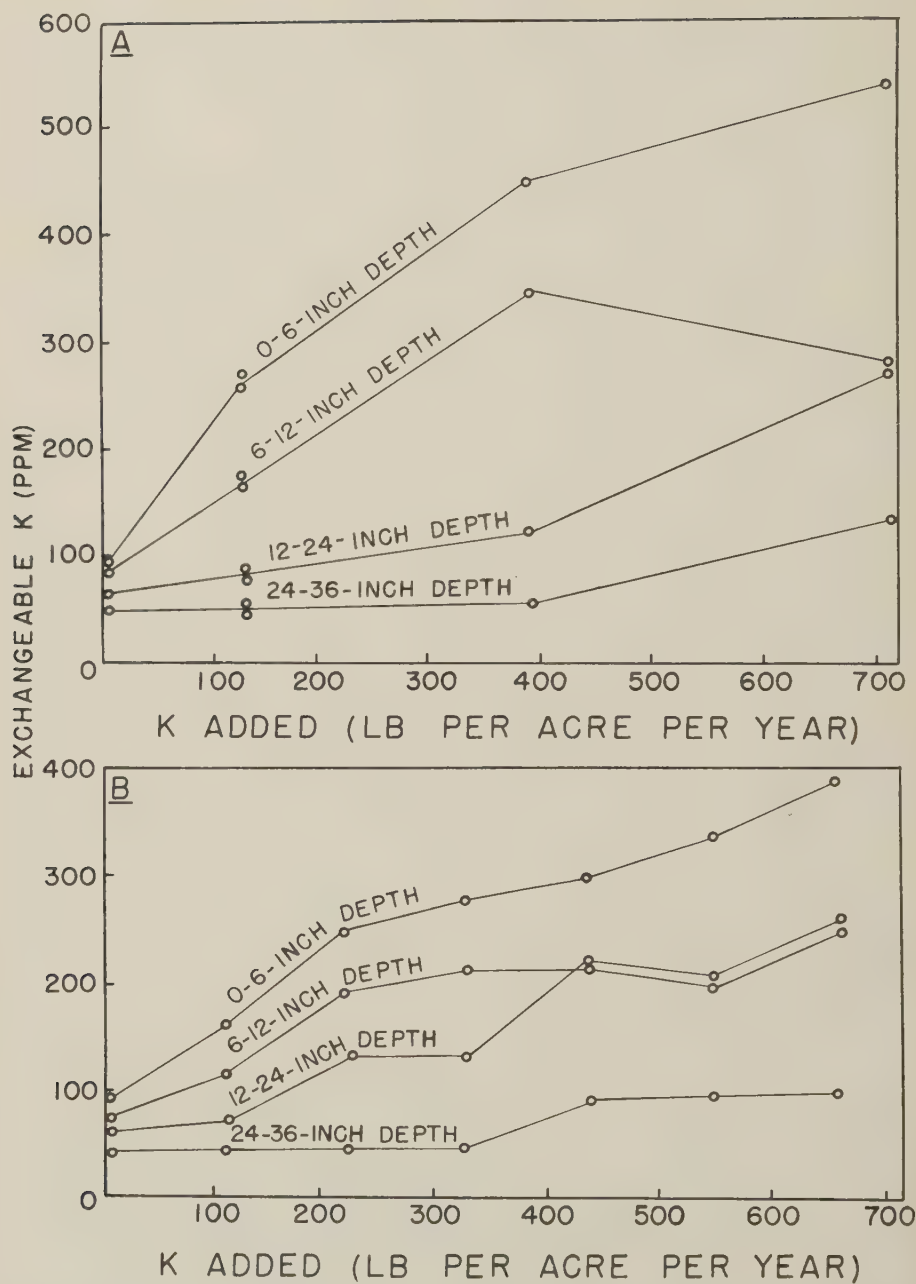


Fig. 7. Relation between exchangeable K in soil samples collected in 1955 and rate of application of K to soil during the period from 1939 to 1955. *A*, K applied as mineral salts; *B*, K applied in manure.

Exchangeable Potassium. Potassium analyses were made by using a Beckman Model DU spectrophotometer with flame photometer attachment. The exchangeable K is that which was removed from the soil with neutral NH_4OAc , and includes the water-soluble K.

The data for exchangeable K in the samples collected in 1955 and in those collected in 1927 show that there was no decrease in the amount of exchangeable K in the soil of any depth in the plots to which no K salts or manure had been added. Thus K release from nonexchangeable forms completely replenished or balanced that which was removed in the fruit or which accumulated under the trees as a result of leaf fall.

Since the levels of exchangeable K in plots that had received no K were the same in 1955 as in 1927, the exchangeable K values in these plots in 1955 were used as a base for estimating the accumulation of exchangeable K in plots that had received applications of K salts and manure.

The relation between the exchangeable K in the soil samples collected in 1955 and the rate of application of K to the soil as mineral salts during the period 1939–1955 are presented in figure 7A and the same relation for K added in manure is presented in figure 7B. The rate of application of K in the manure was calculated from the average content of the manure used during 12 of the twenty-eight years of application. It was assumed that the average K content of the manure used during these twelve years was the same as the average K content would have been if it had been determined each year. The rate of application of K from 1939 to 1955 was used because in some plots the rate of application of manure and K salts was increased, beginning in 1939.

At any given rate of application of K there was more exchangeable K in soil of the 0 to 6 and 6 to 12-inch depths where the K was added as mineral salts than there was where it was added in manure. However, in soil at the 12 to 24-inch depth the reverse was the case. There was more exchangeable K at this depth from the K in manure than from that in the mineral salts. Obviously the K moved into the soil faster where manure had been applied. Water infiltration data showed that the manure increased the amount of water intake per irrigation.

There was no increase in exchangeable K in the soil of the 24 to 36-inch depth until the rate of application exceeded 400 pounds per acre per year. At higher rates of application there were small increases in exchangeable K, indicating that K had moved into this depth. The data for the exchangeable K in the 36 to 48-inch depth, however, indicated that there was little if any penetration of the applied K beyond the 36-inch depth. Thus at rates up to 400 pounds per acre per year, all the applied K can be assumed to have stayed in the first 2 feet of soil, and at higher rates it can be assumed to have stayed in the first 3 feet of soil.

Potassium Fixation. To investigate the K fixation process in this soil, KCl at a rate of 3 me per 100 g was added to samples of soil from the 12 to 24-inch depth of two plots where K salts or manure were not added. Water was added to bring the soil-to-water ratio to 1:1, and the samples were let stand about 16 hours in a moist condition. Some samples were then air-dried, others were oven-dried at 85 °C, and others were allowed to remain moist. All

TABLE 17

FIXATION OF K IN A MOIST CONDITION AND WITH
 DRYING IN SAMPLES OF THE 12-24-INCH DEPTH
 OF SOIL FROM TWO PLOTS OF THE UREA-
 COVERCROP TREATMENT

Treatment of sample in the laboratory	Potassium fixed	
	Plot J-38	Plot M-12
	me/100 g	me/100 g
Moist.....	2.05	1.89
Air dry.....	2.52	2.32
Oven dry.....	2.71	2.64

TABLE 18

FIXATION OF K IN THE MOIST STATE, AGAINST
 EXTRACTION WITH NH_4OAc AND WITH N HCl FOLLOWED
 BY LEACHING WITH BaCl_2 -TRIETHANOLAMINE AT pH
 8.1 PLUS 0.2N BaCl_2 IN THE SAMPLES OF 4 DEPTHS
 OF SOIL FROM A PLOT OF THE UREA-
 COVERCROP TREATMENT

Depth	Fixation against extraction with	
	NH_4OAc	HCl-BaCl_2 - triethanolamine- BaCl_2
	me/100 g	me/100 g
inches		
0-6.....	0.24	0.00
6-12.....	0.50	0.20
12-24.....	1.96	1.83
24-36.....	2.29	2.14

samples were extracted with NH_4OAc ; extracted K was determined, and K fixation was calculated. The data are presented in table 17. The average fixation was 65, 75, and 89 per cent of the K added, for samples that were moist, air-dried, and oven-dried, respectively. Therefore the dominant fixation process is one that takes place under moist conditions, and in the field K fixation can take place rapidly without its being necessary for the soil to become dry.

The objective of the next investigation was to measure K fixation in samples from various depths and K fixation against extraction with NH_4OAc as compared with extraction with the reagents used in the saturation of the soil with Ba in the determination of the cation-exchange capacity. Samples of soil were subjected to the treatment described above, omitting the drying treatments. Data for the K fixation in soil samples from various depths against extraction with NH_4OAc and against extraction with HCl-BaCl_2 -triethanolamine- BaCl_2 are presented in table 18. The surface sample (0 to 6 inches) and the 6 to 12-inch sample fixed little K relative to fixation in the

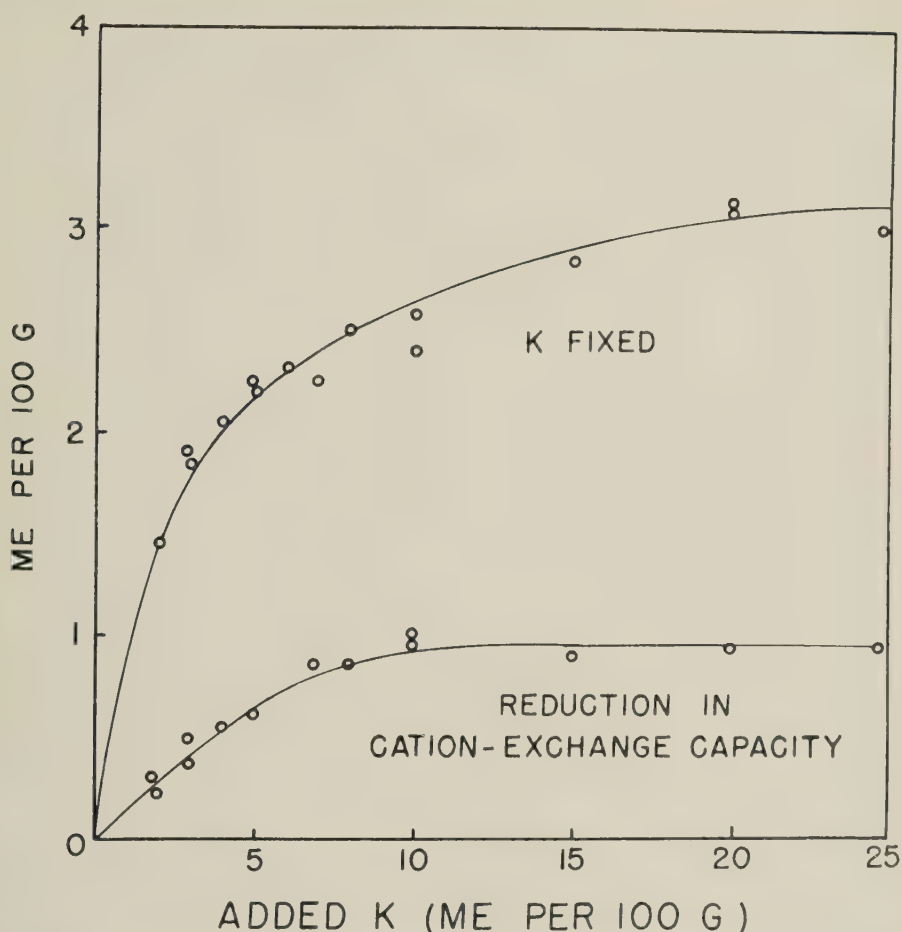


Fig. 8. Relation between K fixation and reduction in cation-exchange capacity and the rate of addition of K in the laboratory to a soil sample from the 12 to 14-inch depth of a plot of the urea-cover crop treatment.

samples from the 12 to 24 and 24 to 36-inch depths. The fixation against extraction with HCl-BaCl_2 -triethanolamine- BaCl_2 was lower than that against extraction with NH_4OAc . The differences were greater in the samples from the 0 to 6 and 6 to 12-inch depths than in those from the 12 to 24 and 24 to 36-inch depths. The extraction of exchangeable K from samples from the same plots showed that the HCl-BaCl_2 -triethanolamine- BaCl_2 extraction replaced more K than the NH_4OAc extraction did, and that the difference was greater in the samples from the surface 0 to 12 inches than in those from the second and third feet of soil.

The relation between reduction in cation-exchange capacity and K fixation in the soil was investigated by measuring these in a moist soil sample from the 12 to 24-inch depth of plot M-12 of the urea-covercrop treatment.

KCl being added at rates ranging from 0 to 25 me per 100 g (fig. 8). The fixed K in this case was that which was retained against extraction with the HCl pretreatment followed by leaching with BaCl_2 -triethanolamine and BaCl_2 solutions. The fixation of K increased to a maximum of about 3 me per 100 g, the percentage fixation decreasing with increase in K added. The reduction in cation-exchange capacity was less than 20 per cent of the K fixation where the added K was 2 me per 100 g, but increased to about 30 per cent at the highest rate of addition of K. There was a high correlation between K fixation and reduction in cation-exchange capacity, but a lack of equivalence and of a constant ratio between the two.

The fixation of K obtained in the field took place at values of exchangeable K of less than 2 me per 100 g, if each yearly application of K is assumed to have been distributed uniformly in the surface 0 to 6 inches of soil. The reduction in cation-exchange capacity in the soil, assuming the ratio of K fixation to reduction of exchange capacity that is shown in figure 8 to obtain in the field, would therefore be so small that it would be masked by the variation from plot to plot in the field. Thus the lack of a reduction in exchange capacity in the soil of plots that have received large amounts of K, as reported previously, is explained.

Part of the K fixed in this soil is probably fixed by a mechanism of entrapment of K ions at exchange sites, with a loss of these sites to exchange reactions. This takes place without drying and loss of water from the soil. The K fixed by this mechanism, however, is about one third or less of the K that is fixed. What other mechanism or mechanisms are responsible for the fixation of the remainder is unknown to the authors. Two recent reviews dealing with K fixation in soil (Kardos, 1955; Reitemeier, 1951) indicate that the mechanism of K fixation is through reduction in cation-exchange sites and that there is an equivalence between K fixation and reduction in cation-exchange capacity. York *et al.* (1953), in a study of the fixation of K induced by liming an acid Mardin silt loam, found no direct relationship between the amount of K entering the exchange complex and the amount of K fixed by the soil in a moist condition. N. J. Volk (1934) and G. W. Volk (1938) had previously postulated that under alkaline conditions the K fixation process is by a combination of K with dissolved Al_2O_3 and SiO_2 to form an insoluble aluminosilicate. Whether this type of fixation is involved in the soil studied for the present report is not known.

Potassium Fixation in the Field. Data for accumulated total K added to the soil, increase in exchangeable K in the soil, estimated K removal from soil by the trees, and the apparent fixation for four treatments are presented in table 19. The K removed in the fruit was calculated by using the actual total weight of harvested fruit and the value of 0.22 per cent K in the fruit. The K in the trees in 1955 was assumed to be of the same order of magnitude as the K content of a 19-year-old grapefruit tree analyzed by Barnette *et al.* (1931), and to vary with the K content of the leaves of the trees in the various treatments. The accumulation of K under the trees from leaf fall was calculated on the assumption that the accumulated K was approximately six times the accumulated P. An estimate of P was obtained from a total analysis of the soil under the trees in the tree row. The apparent K fixation

was the K that was not accounted for in some other manner. It was also assumed that all the K absorbed from the soil by the trees was from the K applied and that there was little if any K release from nonexchangeable forms during the period of the experiment. These last two assumptions are probably more nearly justified in the treatments at the higher rates than in those at the lower rates.

The calculated apparent K fixation, as a percentage of the K added, increased with increase in the amount of K added. In all laboratory studies dealing with K fixation the percentage of fixation has decreased with increase in K added. Thus the data in table 18 represent an unexpected behavior of the applied K. The data, however, are logical when two factors are

TABLE 19

ACCUMULATED TOTAL K ADDED, INCREASE IN EXCHANGEABLE K,
ESTIMATED K REMOVAL FROM THE SOIL BY THE TREES,
AND APPARENT K FIXATION FOR FOUR TREATMENTS

Number	Treatment Description	Accumulated total K added	Increase in exchangeable K in the soil profile	Potassium removal in fruit*	Potassium in trees at present*	Potassium accumulated under trees from leaf fall*	Apparent K fixation†
		lbs/A	lbs/A	lbs/A	lbs/A	lbs/A	lbs/A
5	Urea, K ₂ SO ₄	3,000	588	762	300	1,200	150
10	Urea, phosphate, K ₂ SO ₄ ...	6,700	1,482	802	350	1,300	2,766
42	Urea, manure.....	9,300	890	1,085	400	1,400	5,525
7	Urea, manure, phosphate, KCl.....	17,000	2,500	947	450	1,500	11,603

* Estimated values.

† The total added minus the summation of the increase in exchangeable K, the K removal in fruit, K in trees, and the K accumulation under the trees from leaf fall.

considered: (a) the greater the amount of K added to the soil, the smaller is the proportion used by the trees and the larger the proportion that remains to be fixed; and (b) the soil of the 0 to 12-inch depth fixes very little K, whereas that of the second and third feet fix considerable quantities, and the amount of K that penetrated beyond the 12-inch depth increased with increase in rate of application.

In Treatment 7 the calculated apparent fixation of K was 11.603 pounds per acre, which is in good agreement with the value of 10.360 pounds K fixed in the soil of the same treatment as calculated from total K analyses. This agreement suggests that the values for K fixation in table 18 are reliable, at least at the higher rates of application.

Soluble Copper and Zinc. Soluble Cu and Zn were measured by extracting a 50 g sample of soil with 100 ml of 0.1N HCl. The soil suspension was shaken for 30 minutes and then the soil was removed by filtration. A suitable aliquot was used for Cu and Zn determinations.

Data for soluble Zn in samples from 1927 and 1955 are presented in table 20. The data for 1927 are averages of four plots. The only significant difference in the table is the difference in the surface soil in 1927 and 1955. There has been a large increase in soluble Zn. The source of this increase has been

the Zn sprays that have been applied to the trees. The Zn has accumulated in the treatment that has had no Zn sprays (Treatment 33) to nearly the same level as the other treatments that all received Zn sprays. The drift of the Zn spray from adjacent plots has been sufficient to eliminate Zn deficiency in the trees in this treatment and undoubtedly has produced the large increase in soluble Zn in the surface soil.

TABLE 20
ZINC EXTRACTED BY 0.1N HCl FROM SOIL SAMPLES TAKEN
IN 1927 AND 1955

Treatment		Soluble Zn at indicated depths, inches			
Number	Description	0-6	6-12	12-24	24-36
		ppm	ppm	ppm	ppm
	1927	2.0	...	1.8	1.5
		(0-12 inches)			
	1955				
8	Urea, phosphate.....	22	3.0	3.9	2.9
10	Urea, phosphate, potash.....	21	2.1	1.7	1.9
18	Urea.....	15	1.8	2.0	2.8
26	NaNO ₃	17	1.7	1.3	1.3
30	Manure.....	19	3.3	2.7	3.8
42	Urea, manure.....	20	2.8	1.8	1.6
33	Urea, no Zn sprays.....	13	3.2	2.5	2.9

TABLE 21
THE SOLUBLE Cu AND Zn AND THE ORGANIC C IN THE
SURFACE 6 INCHES OF SOIL FROM PLOTS TREATED
WITH MANURE AT VARIOUS RATES

Treatment number	Rate of application of manure	Organic C	Soluble Cu	Soluble Zn
	lb N/A	per cent	ppm	ppm
18.....	0	0.44	1.9	15
40.....	65	0.69	1.7	19
41.....	130	0.91	1.1	18
14.....	195	1.01	0.65	29
19.....	260	1.12	0.65	22
25.....	335	1.22	0.61	22
30.....	390	1.32	0.24	19

The increase in soluble Zn has been only in the surface 0 to 6 inches of soil. Probably the major portion of this has been in the surface 2 or 3 inches. Thus, the Zn that has gotten into the soil from repeated Zn sprays on the leaves, cannot be expected to have any influence on the Zn availability to citrus trees.

The relation between soluble Cu and Zn, and the organic C content of the samples from soil from the plots where manure was added at various rates is presented in table 21. There was a decrease in soluble Cu as the organic

matter increased. This is in accord with the generally accepted principle that Cu is less available in organic soils than in mineral soils and that the mineral soils with the highest organic matter generally have lower available Cu. There was no consistent effect of organic matter on Zn solubility.

There was no apparent effect of phosphate or potash on the amount of Cu and Zn extracted with 0.1N HCl. There was an effect of pH on Zn (see table 22). The solubility of Zn was low in the soils of the $(\text{NH}_4)_2\text{SO}_4$ treatment (pH = 4.0) and highest at pH values near 6.5. Where lime was added the solubility of both Zn and Cu was decreased. The effect of lime on Cu solubility was greater than its effect on Zn.

TABLE 22

ZINC AND Cu SOLUBLE IN 0.1N HCl AND pH OF THE 0-6 INCHES OF SOIL TAKEN IN 1955 FROM PLOTS OF 11 TREATMENTS

Treatment		pH	Soluble Zn	Soluble Cu
Number	Description			
			ppm	ppm
15	$(\text{NH}_4)_2\text{SO}_4$	4.0	7.8	2.0
22	$(\text{NH}_4)_2\text{SO}_4$	4.0	9.0	1.9
12	Dried blood, $(\text{NH}_4)_2\text{SO}_4$, NaNO_3	5.3	13	1.2
13	Mixed fertilizers.....	5.6	20	1.9
8	Urea, phosphate.....	6.6	22	1.9
18	Urea.....	7.0	15	1.9
15a	$(\text{NH}_4)_2\text{SO}_4$, lime since 1946.....	7.1	14	0.8
22a	$(\text{NH}_4)_2\text{SO}_4$, lime since 1946.....	7.1	14	0.8
11	Urea, potash.....	7.2	17	2.0
16	$(\text{NH}_4)_2\text{SO}_4$, lime since 1927.....	7.6	4.0	0.1
26	NaNO_3	8.5	17	1.5

DISCUSSION

Irrigation water alone produced several changes in this soil during 38 years (1917 to 1955). The pH increased from about 6.8 in 1918 to about 8.0 in 1955. Although there was only a slight increase in salinity as indicated by the conductivity of the saturation extract there was greater than 100 per cent increase in soluble sodium percentage which was 24 per cent in 1918 and 54 per cent in 1955. There was an increase in free lime in the soil of this treatment. The precipitation of CaCO_3 from the Ca and HCO_3 ions of the irrigation water was unquestionably the source of the lime and also explains the increase of soluble sodium percentage to a value of 54 per cent compared to a value of 31 per cent for the irrigation water. The precipitation of Ca and Mg by the HCO_3 had been sufficient to increase the soluble sodium from 31 to 54 per cent. Since the maximum possible sodium percentage, assuming all of the HCO_3 had reacted with Ca and Mg, was 88 per cent, about 60 per cent of the HCO_3 in the water had reacted with Ca and Mg to form a mixed salt of Ca and Mg carbonates.

No accurate estimate of water intake into the soil of the check plots can be obtained. However, from recent estimates of water intake on various plots

in the experiment, we can guess that about 60 acre feet of irrigation water have entered the soil. If 60 per cent of the HCO_3 in this water had reacted with Ca and Mg to form carbonates there should be an accumulation of 14,700 lbs. CaCO_3 or equivalent in the 0 to 36-inch depth of soil. Or, if the water intake had been 50 acre feet, the lime accumulation should be 12,200 lbs. CaCO_3 , or equivalent. The lime accumulation from actual measurement is 10,600 lbs. CaCO_3 or equivalent assuming the weight of 2,000,000 lbs. per acre 6 inches or 13,000 lbs., assuming a weight of 2,500,000 lbs. per acre 6 inches. The soil is relatively sandy and a weight of 2,500,000 lbs. per acre 6 inches is not unlikely. The data are of the same order of magnitude and suggest that a 60 per cent reaction of the HCO_3 for carbonates is a reliable estimate. The data herein presented agree with Eaton (1950) in his introduction of the concepts of residual Na_2CO_3 and possible Na percentage.

Covercrops produced several desirable effects as compared to clean cultivation. The organic C and N contents were slightly higher. The soluble Na percentage and exchangeable Na were lower. The maximum effect of the covercrop in reducing salinity and alkali hazards was in the NaNO_3 and $(\text{NH}_4)_2\text{SO}_4$ treatments where structural deterioration was most severe. Parker and Jones (1952) showed that the yields of navel oranges were greater with the covercrop and here again the maximum effect on yields was with the $(\text{NH}_4)_2\text{SO}_4$ and NaNO_3 treatments where structural deterioration resulted from the effects of the chemicals added.

Because the covercrops reduced salinity in comparison to clean cultivation the benefits derived from them are probably largely a result of greater water penetration. Parker and Jenny (1945) found increased water penetration in the covercrop plots in this fertility trial, and Aldrich *et al.* (1945), in studying soil samples taken in 1943, found that the soils treated with NaNO_3 and $(\text{NH}_4)_2\text{SO}_4$ had much lower water stability and permeability than soils from all other treatments.

Treatment with NaNO_3 produced alkali conditions. The exchangeable Na increased to about 50 per cent of the cation-exchange capacity in soil of the 12 to 24 and 24 to 36-inch depths, and the soluble Na increased to 91 per cent in the 12 to 36-inch depth. Treatment with gypsum from the beginning of the use of NaNO_3 was effective in preventing alkali conditions. The rate of application of gypsum in this case was one ton per acre per year. Treatment with gypsum starting in 1946 reduced exchangeable Na to about 20 and 33 per cent of the values in the NaNO_3 treatment in the 0 to 12 and 12 to 36-inch depths, respectively. Thus, the alkali condition resultant from the use of NaNO_3 in this soil, is easily eliminated.

Treatment with $(\text{NH}_4)_2\text{SO}_4$ produced rather extreme acidification of the 0 to 24-inch depth of soil. At the rate of application of N during the period from 1927 to 1938 inclusive, (1 lb. per tree per year) there was little if any acidification. It was only when the rate of N application was increased to 3 lbs. per tree per year (starting in 1939) that acidification became a problem. Associated with acidification with $(\text{NH}_4)_2\text{SO}_4$ was an accumulation of exchangeable NH_4 in the surface soil. Lime was effective in eliminating all the undesirable effects produced by this acidification.

Mineral N supplied along with covercrops and alfalfa hay, bean straw, and cereal straw apparently had little effect on retention of carbon from these sources. The organic C and N were only slightly higher in the soils where these materials were added along with covercrop than they were in soils where the covercrop was used alone, whereas an equivalent amount of organic matter in manure gave relatively large increases in organic C and N.

According to various investigators, the addition of N to crop residues has the effect of increasing C retention. The results of the present studies do not support this view. Bartholomew (1955) has reviewed the data of 10 decomposition studies which were continued for more than a year. He found that in three of these studies added N had no measurable effect on C retention, while in three studies added N decreased C retention. Bartholomew stated that N fertilizers are most advantageously used, not only for crop production, but also for building soil organic matter, when properly applied to the crop to produce maximum economic yields, and that the process of decomposition of organic residues cannot be altered enough by the addition of N to make the effort worth while.

The data pertaining to accumulation of P and K in this soil agree well with the well-known fact that both P and K added to the surface soil move relatively slowly into the lower depths. The movement is so slow that once excessive amounts of these two elements have accumulated, many years may be required to remove them from the surface soil. Also, several years may be required before chemical fixation reduces excessive solubility of these elements. Considering the fact that P and K accumulate in an available form from repeated applications, the nonleachability of these elements, and the undesirable secondary or direct effects of accumulations, repeated application of phosphates or potash should be avoided unless evidence is available to indicate that these are essential for continued high yields of crops.

The decrease in exchangeable Mg in the soil of this fertility trial cannot be assumed to have resulted from leaching alone. Approximately 40 lbs. Mg per acre were removed in the fruit, and about 380 lbs. Mg per acre were estimated to have been absorbed by the trees. Some Mg has undoubtedly been deposited along with Ca in the form of carbonates (there was an accumulation of lime in the soil). However, the removal by the trees and precipitation as a carbonate cannot be expected to have caused the high correlation between decrease in exchangeable Mg and the pound-equivalents of salts added. Thus, we can assume that the decrease in exchangeable Mg was mainly a result of leaching losses. Another unknown factor in the balance of Mg in this soil is the release from primary and secondary minerals. The losses by leaching could have been much larger if release from nonexchangeable forms balanced part of the loss.

The loss of Mg in this soil has not produced Mg deficiencies. However, with a longer period of use of fertilizers and soil amendments, and continued leaching, Mg deficiencies will undoubtedly develop unless Mg is added to the fertility program. There has been increasing evidence of Mg deficiencies in soils of southern California. One cause of this increase is probably the loss of Mg through continued use of fertilizers and soil amendments.

SUMMARY

Some chemical changes that have occurred during thirty-eight years of irrigation and growth of citrus, and twenty-eight years of differential fertilization of a Ramona sandy loam have been reported and discussed. The following paragraphs summarize the results.

Acidity and Alkalinity. Irrigation water increased the alkalinity of the soil. The effect of fertilizers varied from extreme acidification with high rates of $(\text{NH}_4)_2\text{SO}_4$ to extreme alkalinization with NaNO_3 .

Lime Accumulation. There was an increase in lime content except where $(\text{NH}_4)_2\text{SO}_4$ acidified the soil. The accumulation was greatest in the 0 to 6 and 24 to 36-inch depths with a minimum at the 6 to 12-inch depth.

Salinity. There was a small increase in salinity from irrigation water alone. Treatment with $(\text{NH}_4)_2\text{SO}_4$ or with NaNO_3 produced high salinity. The yield of navel orange fruits was negatively correlated with the conductivity of the saturation extract.

Organic Carbon. Treatment with manure increased the organic C in the 0 to 6-inch depth but had no effect at other depths. Other treatments had only small effects.

Phosphorus. Acidifying treatments increased the soluble P. More than 60 per cent of the P added as triple superphosphate accumulated in the surface 6 inches, and greater than 80 per cent was retained in the 0 to 12-inch depth.

Cation-Exchange Capacity and Exchangeable Cations. The cation-exchange capacity was positively correlated with organic C in the soil. About half or more of the cation-exchange capacity of the surface soil was associated with organic matter. Where the soil became acid the exchange acidity displaced mainly Ca. Where exchangeable Na increased there was a corresponding decrease in exchangeable Ca. Exchangeable Mg was depleted in proportion to the amounts of salts added as fertilizers and soil amendments.

Potassium. Potassium fixation was mainly in the soil below the 12-inch depth. The per cent of the applied K that was fixed into nonexchangeable forms increased with increase in rate of K application.

Soluble Copper and Zinc. The soluble Zn was low in extremely acid soil and soil treated with lime, and was highest at pH values near 6.5 where no lime was added. Soluble Cu was lowest where lime was added but pH, per se, had no effect. Soluble Cu decreased with increase in organic C.

LITERATURE CITED

- ALDRICH, D. G. JR., E. R. PARKER, and H. D. CHAPMAN
1945. Effects of several nitrogenous fertilizers and soil amendments on the physical and chemical properties of an irrigated soil. *Soil Sci.* 59: 299-312.
- ALLISON, F. E., and E. M. ROLLER
1955. A comparison of leaching and distillation procedures for determining fixed ammonia in soils. *Soil Sci.* 80: 349-62.
- BARNETTE, R. M., E. F. DEBUSK, J. B. HESTER, and H. W. JONES
1931. The mineral analysis of a nineteen-year-old Marsh seedless grapefruit tree. *Citrus Indus.* 12: 5-6, 34.
- BARTHOLOMEW, W. V.
1955. Fertilization of crop residues. Does it pay? *Agr. Chem.* 10: 38-40, 97.
- BROADBENT, F. E.
1953. The soil organic fraction. *Advances in Agron.* 5: 153-83.
- BURD, J. E.
1948. Chemistry of phosphate ion in soil systems. *Soil Sci.* 65: 227-47.
- CHAPMAN, H. D.
1934. The phosphate of southern California soils in relation to citrus fertilization. *California Agr. Exp. Sta. Bul.* 571.
- CHENERY, E. M.
1948. Thioglycolic acid as an inhibitor for iron in the colorimetric determination of aluminum by means of "aluminon." *Analyst* 74: 501.
- DEAN, L. A.
1938. An attempted fractionation of soil phosphorus. *Jour. Agr. Sci.* 28: 234-46.
- DICKMAN, S. R., and R. H. BRAY
1940. Colorimetric determination of phosphate. *Indus. and Engin. Chem. Analyt. Ed.* 12: 665-68.
- EATON, F. M.
1950. Significance of carbonates in irrigation water. *Soil Sci.* 69: 123-33.
- HARDING, R. B., P. F. PRATT, and W. W. JONES
1958. Changes in salinity, nitrogen, and soil reaction in a differentially fertilized irrigated soil. *Soil Sci.* 85: 177-84.
- KARDSO, L. T.
1955. Soil fixation of plant nutrients. *Amer. Chem. Soc. Monograph* 126: 177-99.
- MCCOLLOCH, R. C., F. T. BINGHAM, and D. G. ALDRICH
1957. Relation of soil potassium and magnesium to magnesium nutrition of citrus. *Soil Sci. Soc. Amer. Proc.* 21: 85-88.
- MEHLICH, A.
1948. Determination of cation- and anion-exchange properties of soils. *Soil Sci.* 66: 424-445.
- MEHTA, N. C., J. O. LEGG, C. A. I. GORING, and C. A. BLACK
1954. Determination of organic phosphorus in soils: I. Extraction method. *Soil Sci. Soc. Amer. Proc.* 18: 443-49.
- OLSEN, S. R., C. V. COLE, FRANK WATANABE, and L. A. DEAN
1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. *U. S. Dept. Agr. Cir.* 939.
- PARKER, E. R., and H. JENNY
1945. Water infiltration and related soil properties as affected by cultivation and organic fertilization. *Soil Sci.* 60: 353-76.
- PARKER, E. R., and L. D. BATCHELOR
1932. Variations in the yields of fruit trees in relation to the planning of future experiments. *Hilgardia* 7: 81-161.
- PARKER, E. R., and L. D. BATCHELOR
1942. Effect of fertilizers on orange yields. *California Agr. Exp. Sta. Bul.* 673.
- PARKER, E. R., and W. W. JONES
1951. Effect of fertilizers on yields, size and quality of orange fruits. *California Agr. Exp. Sta. Bul.* 722.

PRATT, P. F.

1957. Effect of fertilizers and organic materials on the cation-exchange capacity of an irrigated soil. *Soil Sci.* **83**: 85-89.

PRATT, P. F., and BENOIST GOULBEN

1957. Potassium fixation in soil of a long-term fertility trial with citrus. *Soil Sci.* **84**.

PRATT, P. F., BENOIST GOULBEN, and R. B. HARDING

1957. Changes in organic carbon and nitrogen in an irrigated soil during 28 years of differential fertilization. *Soil Sci. Soc. Amer. Proc.* **21**: 215-19.

PRATT, P. F., and R. B. HARDING

1957. Effect of fertilizers on loss of magnesium from soil. *Agron. Jour.* **49**: 419-21.

PRATT, P. F., N. HOLOWAYCHUK, and H. H. MORSE

1955. Soluble phosphorus in soils of Ohio. *Ohio Agr. Exp. Sta. Res. Cir.* **27**.

PRATT, P. F., W. W. JONES, and H. D. CHAPMAN

1956. Changes in phosphorus in an irrigated soil during 28 years of differential fertilization. *Soil Sci.* **82**: 295-306.

REITEMEIER, R. F.

1946. Effect of moisture content on the dissolved and exchangeable ions of the soil of arid regions. *Soil Sci.* **61**: 195-214.

1951. Soil potassium. *Advances in Agron.* **8**: 113-64.

SHELTON, W. R., and H. J. HARPER

1940. A rapid method for the determination of total phosphorus in soils and plants. *Iowa State Coll. Jour. Sci.* **15**: 403-13.

SPENCER, W. F.

1957. Distribution and availability of phosphates added to a Lakeland fine sand. *Soil Sci. Soc. Amer. Proc.* **21**: 141-44.

STELLEY, M., and W. H. PIERRE

1943. Forms of inorganic phosphorus in the C horizons of some Iowa soils. *Soil Sci. Soc. Amer. Proc.* (1942) **7**: 139-47.

STEPHENSON, R. E., and H. D. CHAPMAN

1931. Phosphate penetration in field soils. *Amer. Soc. Agron. Jour.* **23**: 759-70.

U. S. SALINITY LABORATORY STAFF

1954. Diagnosis and improvement of saline and alkali soils. U. S. Dept. Agr. Handbook No. 60. U. S. Government Printing Office, Washington, D.C.

VOLK, G. W.

1938. The nature of potash fixation in soils. *Soil Sci.* **45**: 263-76.

VOLK, N. J.

1934. The fixation of potash in difficultly available form in soils. *Soil Sci.* **37**: 267-87.

WALKLEY, A., and I. A. BLACK

1934. An examination of the Degtjarell method of determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil Sci.* **37**: 29-38.

YORK, E. T. JR., RICHARD BRADFIELD, and MICHAEL PEECH

1953. Calcium-potassium interactions in soils and plants: I. Lime-induced potassium fixation in Mardin silt loam. *Soil Sci.* **76**: 379-87.